Precipitation Kinetics Option for the EQ6 Geochemical Reaction Path Code

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Contents

Glossary of Symbols

a	(a) Thermodynamic activity. (b) edge length of a cube.
A	(a) Thermodynamic affinity. (b) Compound parameter in Appendix C.
A_+	Thermodynamic affinity of a reaction for the forward direction (dissolution); $A_+ = RT \ln (K_+/Q_+)$.
A_-	Thermodynamic affinity of a reaction for the reverse direction (precipitation); $A_- = -A_+$.
B	Compound parameter in Appendix C.
c	Molarity (moles of solute per liter of solution).
c^{eq}	Equilibrium value of c.
c^T	Total concentration (molar).
C	Compound parameter in Appendix C.
D	Diameter of a sphere.
E_a	Activation energy.
$E_{a,+}$	Activation energy (forward direction).
$E_{a,-}$	Activation energy (reverse direction).
f_j	Ratio of active to total surface area.
H_a	Activation enthalpy.
$H_{a,+}$	Activation enthalpy (forward direction).
$H_{a,-}$	Activation enthalpy (reverse direction).
i	Index used for the number of parallel mechanisms, or for a specific species.
$i_{T,j}$	The number of mechanistic terms appearing in the jth irreversible reaction.
j	Subscript used to denote varibles associated with the jth irreversible reaction.
k_+	Rate constant for the forward direction (dissolution).
k_-	Rate constant for the reverse direction (precipitation).
k_p	Precipitation rate constant, Eq. 3-31 (see text).
$k_{T,j,i}$	Index used for the number of activity factors appearing in the ith mechanism of the jth irreversible reaction.
K_+	Equilibrium constant for a reaction (forward direction).
K_-	Equilibrium constant for a reaction (reverse direction); $K = 1/K_+$.
K'_+	Apparent equilibrium constant for a reaction (forward direction).
K'_-	Apparent equilibrium constant for a reaction (reverse direction).
l	Subscript denoting a liquid.
m	(a) Molality. (b) Stoichiometric factor appearing in transition-state theory rate laws ($m = 1/\sigma$).
m^{eq}	Equilibrium value of m (molal concentration).
m^{ss}	Steady-state value of m (molal concentration).
m^o	Initial value of concentration (molal).
m^T	Total concentration (molal).
m_+	Kinetic molal concentration product for reactants (including catalysts).
m_-	Kinetic molal concentration product for products (including catalysts).
M_+	Molal concentration product for a reaction (forward direction).
M_-	Molal concentration product for a reaction (reverse direction).
n	(a) Mass, in moles. (b) Exponential constant appearing in some rate laws. (c) The number of moles of a catalyst appearing in a microscopic reaction.
P	Pressure (bars).
pH	$-\log a_{H+}$.
q_+	Kinetic activity product for reactants (including catalysts).
q_-	Kinetic activity product for products (including catalysts).
Q_+	Ion activity product for a reaction in the forward direction (mineral dissolution).
Q_-	Ion activity product for a reaction in the reverse direction (mineral precipitation). $Q_- = 1/Q_+$.
R	The gas constant (1.98726 cal/mol K).
s	(a) Surface area^2 (cm). (b) Subscript denoting a solid. (c) in V_s, subscript denoting the aqueous solution.

S_j	(See definition of j).
$s_{\#}$	Specific surface area (cm^2/g).
t	Time (usually in seconds).
T	(a) Absolute temperature (K). (b) Superscript denoting a "total" quantity (usually total concentration).
v	Overall velocity of irreversible reactions ($d\xi/dt$).
v_j	Velocity of the jth irreversible reaction ($d\xi_j/dt$).
v_j^{rel}	Relative velocity of the jth irreversible reaction ($d\xi_j/\xi$).
V_a	Activation volume.
$V_{a,+}$	Activation volume (forward direction).
$V_{a,-}$	Activation volume (reverse direction).
V_s	Volume of aqueous solution (liters).
w	Subscript denoting water.
w_w	Mass of water (solvent; kilograms).
*	Superscript denoting the activated complex or a property related to the activated complex.
+	Subscript indicated the forward direction of a reaction.
−	Subscript indicating the reverse direction of a reaction.
γ	Molal activity coefficient of an aqueous solute species.
γ_+	Kinetic activity coefficient product for reactants.
γ_-	Kinetic activity coefficient product for products.
Γ_+	Activity coefficient of a reaction (forward direction).
Γ_-	Activity coefficient of a reaction (reverse direction).
ΔH_+^*	Activation enthalpy (forward direction).
ΔH_-^*	Activation enthalpy (reverse direction).
$\Delta H^\circ_{r,+}$	Standard partial molal enthalpy of reaction (forward direction).
$\Delta V^\circ_{r,+}$	Standard partial molar volume of reaction (forward direction).
ξ	Overall reaction progress variable.
ξ_j	Reaction progress variable for the jth irreversible reaction.
v_{ij}	Stoichiometric reaction coefficient of the ith species in the jth reaction.
ρ	Density (g/cm^3).
σ	Kinetic stoichiometric coefficient [see definition (b) of m].
Ω	The number of moles of water in a mass of one kilogram; approximately 55.51.

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Abstract

The EQ6 reaction path code, which calculates simulations of reactions in aqueous systems, has been modified to permit the modeling of mineral growth kinetics. This modeling option complements a pre-existing capability that allows mineral dissolution kinetics to be calculated. Before this option was added, mineral precipitation in EQ6 was required to follow instantaneous saturation equilibrium. A review of the rate laws pertaining to mineral precipitation and dissolution has led to several rate laws for precipitation, paralleling those for dissolution being programmed into EQ6. Included are rate laws for transition-state theory expressions and "activity-term" expressions. To use the modeling option, EQ6 users must choose an appropriate rate law and provide the necessary constants for each kinetically governed reaction in the input file. Additional rate laws can be added with little difficulty. We have excercised the new capability for some relatively simple cases and partially verified it against closed-form solutions for cases of precipitation and recrystallization of pure silica phases. This capability facilitates the extrapolation and testing of rate laws in systems where precipitation is important, including the case of mineral transformations involving coupled dissolution and precipitation. It also permits more realistic simulation modeling of relatively short-term rock/water interaction experiments and of long-term interactions that are inaccessible by experiment.

1. Introduction

This report describes the addition of a general capability for treating precipitation growth kinetics to the EQ6 reaction path code. It also describes the specific rate laws that have been incorporated into the code. EQ3/6 is a software package consisting of several related FORTRAN computer codes and data files for use in geochemical modeling of aqueous systems (Wolery, 1979, 1983, 1986a; Wolery et al., 1985; Delany and Wolery, 1984). In all previously released versions of EQ6, the treatment of actual kinetics was restricted to the dissolution of solid phases. The new option incorporates rate laws for precipitation that can be used in a manner similar to the existing rate laws for dissolution. Precipitation kinetics enables EQ6 users to model geochemical interactions more realistically in a wide range of aqueous environments. This is especially important in modeling solid/water interaction experiments in the laboratory, where time frames are relatively short.

In heterogenous aqueous systems (solids and water), precipitation from solution occurs either by growth on existing surfaces or by nucleation. The precipitation kinetics option described in this report includes only the first process. Simplified treatments of nucleation processes are planned for future addition to the code. Homogeneous reactions in aqueous solutions, such as metal complexation and ligand protonation processes, are usually fast, with most having half times of less than 1 s. Thus, assuming that such reactions can be modeled, instantaneous thermodynamic equilibrium is usually appropriate for most geochemical calculations. In contrast, the heterogeneous processes of precipitation and dissolution tend to occur on longer time scales, and the assumption of

instantaneous equilibrium for such reactions in geochemical calculations is often not adequate. Thus, the addition of precipitation kinetics to EQ6 should greatly improve our ability to model natural aqueous systems.

The time scales for most applications of geochemical modeling range from a fraction of a day up to a hundred thousand years or so. If a reaction equilibrates rapidly in a few minutes or hours, it can usually be modeled by assuming instantaneous solubility equilibrium. The rate at which a mineral dissolves or precipitates is controlled by a minimum time scale imposed by the need for aqueous components to diffuse between the mineral surface and the bulk volume of solution. This rate is usually fast enough to render the assumption of instantaneous solubility equilibrium, adequate for most geochemical calculations, if it indeed controls the rate of reaction as it often does for highly soluble salts such as halite (NaCl). Aqueous diffusion is otherwise able to control reaction rates only when the diffusion distances involved are substantial (on the order of meters to tens of meters). Such a scenario requires a coupled geochemistry/transport code and lies outside the current scope of EQ6.

This document focuses mainly on the dissolution and precipitation reactions controlled by surface chemistry kinetics. The general importance of such mechanisms for controlling mineral dissolution kinetics in geochemical processes has been established only within the past several years (see Holdren and Berner, 1979; Berner and Holdren, 1979; Berner, 1981; Lasaga, 1981a, 1984). A similarly important role of these processes can be inferred for mineral precipitation mechanisms. If equilibrium is defined as a steady-state condition, it can be considered a balance of equal dissolution and precipitation rates (Lasaga, 1981a). Although a significant amount of data is not available to model the precipitation of specific minerals, we hope that the incorporation of this option into EQ6 will encourage and support the generation of such data. New measurements to determine kinetic data for both dissolution and precipitation processes are critical if state-of-the-art geochemical modeling is to progress significantly beyond equilibrium modeling.

This expansion of EQ6 was supported by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This project has adopted EQ3/6 for application to problems concerning the disposal of high-level nuclear waste in a proposed underground repository in tuff in the state of Ne-

vada. Code development is determined by project needs as defined in the EQ3/6 Geochemical Modeling Plan (McKenzie et al., 1986), not by the availablility of data needed to support the calculations. Project needs include characterizing the host-rock environment, identifying the factors that affect groundwater transport of radionuclides into the accessible environment, and predicting the chemical interactions that are expected to occur because of temperature perturbations in and about the repository. They also include general predictions and estimates of the geochemical conditions expected in an underground high-level nuclear waste repository.

This kinetics option is probably being released ahead of its usefulness to most of the EQ3/6 user community because rate-constant data exist for only a few minerals. Nevertheless, it provides a tool for predicting the results of laboratory experiments, and it may facilitate the testing of different theories for mineral precipitation. We hope that more research on the mechanisms of heterogeneous processes (e.g., incongruent dissolution; the growth and nucleation of thermodynamically favored, often kinetically slow phases; and the rapid precipitation from solution of amorphous or thermodynamically metastable crystalline phases) will become available. At present, rate constants have been determined using experimental data for relatively few rock-forming minerals (for either dissolution or precipitation). For this study, available data include those for the silica phases (Rimstidt and Barnes, 1980), calcium carbonate (cf. Busenberg and Plummer, 1982, and references therein), and albite (Knauss and Wolery, 1986, and references therein).

The kinetic precipitation rate laws incorporated into the EQ6 code parallel the dissolution rate laws included in the previously released 3175 and 3230 versions of the EQ3/6 package (see Wolery, 1986a). The 3245 version of the EQ6 code, which contains the precipitation kinetics capability, is planned for release in 1987. The rate law expressions incorporated into EQ6 were chosen to be representative of the most useful reported forms to which experimental data have been fit. Some of these rate laws are largely empirical in nature, while others have more of a basis in theory. In many cases, reported rate data can be equally well supported by using more than one interpretation of the reaction mechanism and the subsequent rate law. The incorporation of any rate law into the EQ6 code does not necessarily constitute endorsement by the authors. Some rate laws

have been added primarily to allow the reproduction of observed experimental data and/or to facilitate comparisons with results obtained using other rate laws.

Several computer codes that make kinetic calculations in homogeneous systems (a gas phase, an aqueous solution, etc.) have been described in the literature (e.g., CHEMKIN, Kee et al., 1980; KINRATE AND KINBOX, Uhlen and Edsberg, 1979). Some of these codes are widely used in modeling the chemistry of combustion and of parts of the earth's atmosphere. A general computer code for treating heterogeneous kinetics, particularly one capable of handling aqueous systems, has yet to be described in the literature, although a few codes with limited capabilities now exist (e.g., RATECALC, mentioned by Plummer et al., 1979; an early modified version of EQ6 that does dissolution kinetics only, Helgeson and Murphy, 1983; PROTOCOL, with the same limitation, Jackson, 1984; a modified version of PHREEQE, Grambow, 1985).

Precipitation in geochemical reaction path codes has traditionally been treated as an equilibrium saturation phenomenon. Primary solids dissolve irreversibly (i.e., kinetically, not according to equilibrium), and all secondary solids precipitate reversibly (i.e., according to equilibrium); see Helgeson (1968). Most codes built around this concept permit the user to suppress the precipitation of selected phases, allowing the aqueous solution to become supersaturated. However, this is generally the only permissible alternative to instantaneous equilibrium.

2. Reactions, Thermodynamic Properties, and Rates

Each mineral in the EQ3/6 database has an associated macroscopic reaction (Wolery, 1983, 1986a). This reaction is stored in the data file, with the mineral always appearing as a reactant. An example of such a reaction is the dissolution of albite:

$$NaAlSi_3O_8(c) + 4 H^+ = Na^+ + Al^{3+}$$

$$+ 3 SiO_2^{\circ} + 2 H_2O \quad . \quad (2\text{-}1)$$
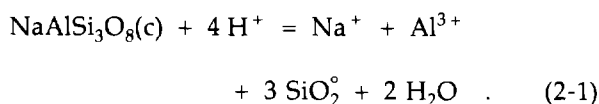
The stoichiometric coefficients (symbolized below by v_{ij}, where i denotes the species and j the reaction) are represented in the data file and the EQ3/6 codes, following the convention that v_{ij} is negative for reactants and positive for products. The reaction (Eq. 2-1) represents mineral dissolution and corresponds to the forward direction for all reactions. The reverse reaction corresponds to precipitation.

The thermodynamic aspects of macroscopic reactions necessary to a discussion of reaction kinetics are reviewed briefly below (for a complete review, see Wolery, 1986b). Equilibrium requires that

$$Q_+ = K_+ \quad , \quad (2\text{-}2)$$

where Q is the ion activity product for the reaction, K is the corresponding equilibrium constant, and the "+" subscript denotes that these quantities correspond to the forward reaction direction. Q_+ is given by

$$Q_+ = \prod_i a_i^{v_i} \quad , \quad (2\text{-}3)$$

where a_i is the thermodynamic activity of the ith species in the reaction. The thermodynamic driving force of a reaction can be expressed by the affinity

$$A_+ = RT \ln(Q_+/K_+) \quad , \quad (2\text{-}4)$$

where R is the gas constant and T is the absolute temperature. Thus, the condition for equilibrium can also be written

$$A_+ = 0 \quad . \quad (2\text{-}5)$$

The previous equations also hold for the reverse reaction, in which each "+" subscript is subsequently replaced by "−" and the equations are written in terms of the corresponding parameters. These parameters are related to each other by

$$Q_- = \frac{1}{Q_+} \quad , \quad (2\text{-}6)$$

$$K_- = \frac{1}{K_+} \quad , \quad (2\text{-}7)$$

and

$$A_- = -A_+ \quad .\tag{2-8}$$

Rates of mineral dissolution and/or precipitation in aqueous systems are often described in the literature in terms of the rate of change of concentration of an aqueous species produced or consumed in the process. In the EQ6 code, concentration is expressed as molal concentration (m), moles of substance per kilogram of solvent water. The literature also makes considerable use of molar concentration (c), moles of substance per liter of solution. Molality has a substantial advantage over molarity in the treatment of aqueous systems because the use of molarity over wide ranges of temperature, pressure, and solute content requires a model of how the solution volume varies with changes in these parameters. At temperatures near 25°C and in dilute solutions, the two measures of concentration are nearly equal. Thus, results reported as molarity may be taken as molality with usually negligible error.

The molality of solute i (m_i) is related to the mass of i (n_i) by

$$m_i = \Omega n_i / n_w \quad ,\tag{2-9}$$

where Ω is the number of moles of water composing a mass of 1 kg ($\Omega \simeq 55.51$) and n_w is the number of moles of water. Differentiating with respect to time gives

$$dm_i/dt = \left(\frac{\Omega}{n_w}\right)\left[dn_i/dt - \left(\frac{n_i}{n_w}\right)dn_w/dt\right] \quad ,\tag{2-10}$$

where dn_i/dt and dn_w/dt describe the rate of change as a function of time of the mass of the ith species and water, respectively. The rate of change in the mass of the ith species can be caused by an outside reaction. For the jth reaction, this can be written as

$$\left(dn_i/dt\right)_j = v_{ij}v_j \quad ,\tag{2-11}$$

where v_{ij} is the stoichiometric reaction coefficient, and v_j is the reaction velocity of the jth reaction. For more than one simultaneous reaction,

$$dn_i/dt = \sum_{j=1}^{j_T} v_{ij}v_j \quad .\tag{2-12}$$

Substituting Eq. 2-12 into Eq. 2-10 for both the ith solute and solvent, water, we obtain

$$dm_i/dt = \left(\frac{\Omega}{n_w}\right)\sum_{j=1}^{j_T}\left[v_{ij} - \left(\frac{v_{wj}n_i}{n_w}\right)\right]v_j \quad .\tag{2-13}$$

For the molar concentration of solute i given by

$$c_i = n_i/V_s \quad ,\tag{2-14}$$

where V_s is the volume of solution in liters, further substitution leads to considerably more complicated expressions. See Wolery (1986b) for an analog to Eq. 2-13.

The rate of a reaction is represented precisely by the reaction velocity, v_j, and only indirectly by dm_i/dt (or dc_i/dt) or even dn_i/dt. The first reason for this is that more than one reaction may contribute to the overall rate of change in the concentration or mass of a species. The second is that these parameters are further affected by the rate of change in solvent mass (or V_s when units of concentration are expressed in molarity). In mineral dissolution or precipitation kinetics experiments, solvent mass is one of the indirect quantities that is actually measured. Useful results can normally be obtained when only one reaction contributes to the measurements and when the solvent mass or solution volume is relatively constant. Although a relatively constant solvent mass or solution volume is usually obtainable, the former requires that the precipitation of unwanted phases be avoided and is more difficult to achieve. If these conditions are satisfied,

$$v_j \simeq \frac{n_w}{\Omega v_{ij}} dm_i/dt\tag{2-15}$$

and

$$v_j \simeq \frac{V_s}{v_{ij}} dc_i/dt \quad .\tag{2-16}$$

The reaction velocity is formally defined as

$$v_j = d\xi_j/dt \quad ,\tag{2-17}$$

where ξ_j is the reaction progress variable for the jth reaction and t is time. In EQ6, the reaction progress variables measure the extent to which a reaction has proceeded. ξ is used for reactions that are irreversible (not at equilibrium). Individual irreversible reactions can be combined to form an overall irreversible reaction progress variable (ξ), defined by

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$$\xi = \sum_{j=1}^{j_T} |\xi_j| \quad .\qquad (2\text{-}18)$$

Differentiating this equation with respect to time yields an overall reaction rate (v), defined as

$$v = \sum_{j=1}^{j_T} |v_j| \quad .\qquad (2\text{-}19)$$

The use of absolute values in Eqs. 2-18 and 2-19 differs from the equations given by Helgeson (1968), Wolery (1979), and Helgeson and Murphy (1983). These earlier treatments of irreversible reactions did not take account of sets of reactions with both positive and negative reaction velocities. Consider a case involving two irreversible reactions. If v_1 is positive and $v_2 = -v_1$, then Eq. 2-19 gives $v = 2\,v_1$, which is physically reasonable. Without the absolute value constraint, a value of $v = 0$ would be physically unreasonable.

The relative rate of the jth irreversible reaction can defined by

$$v_j^{\text{rel}} = d\xi_j / d\xi \quad .\qquad (2\text{-}20)$$

Relative rates are calculated in EQ6 for all irreversible reactions. Assuming that a kinetic rate law is specified for the jth irreversible reaction,

$$v_j^{\text{rel}} = v_j / v \qquad (2\text{-}21)$$

(hence the importance of avoiding the condition $v = 0$). In EQ6, mass transfer is accomplished by the advancement of ξ and by integrating the relative rates with respect to it (see Wolery, 1986b). The time is calculated analogously by integrating the inverse rate (Helgeson and Murphy, 1983), which is defined by

$$dt/d\xi_j = 1/v \quad .\qquad (2\text{-}22)$$

In EQ6, the "reaction progress mode" does not operate with a time variable. Relative reaction velocities are specified directly by the user in the form

$$v_j^{\text{rel}} = k_{-,1} + k_{+,2}\,\xi + \frac{1}{2}k_{+,3}\,\xi^2 \quad .\qquad (2\text{-}23)$$

This form bears no particular theoretical significance and is a truncated, second-order Taylor's series (Wolery, 1986b). Relative rates defined in this manner are usually treated as constants (i.e., using only the first term in Eq. 2-23), a method that has been used since the early days of reaction path modeling (Helgeson, 1968). An analogous treatment can be made for the reverse direction to represent relative precipitation rates:

$$-v_j^{\text{rel}} = k_{-,1} + k_{-,2}\,\xi + \frac{1}{2}k_{-,3}\,\xi^2 \quad .\qquad (2\text{-}24)$$

EQ6 uses the following procedure to handle both kinetic and relative reaction rates. At the beginning of each progressive step in the reaction, EQ6 calculates rate values (v_j) for all irreversible reactions for which actual rate laws are specified on the input file. Then it calculates the overall rate (v) from Eq. 2-19, excluding the irreversible reactions for which relative rate law expressions were given. This allows the corresponding relative rates (v_j^{rel}) to be calculated according to Eq. 2-21 and the inverse rate $(1/v)$ to be calculated according to Eq. 2-22. It then calculates the relative rates for the remaining irreversible reactions, according to Eq. 2-23 or 2-24, and inverts Eq. 2-21 to obtain the corresponding actual rates (v_j). Calculations involving mixed relative and actual rate law specifications lose their time frame if all rates specified by actual rate laws reduce to zero either by equilibration or exhaustion of the necessary components.

3. Review of Rate Laws for Precipitation and Dissolution

The kinetics of precipitation and dissolution are so intertwined that both are included in the following discussion. A wide variety of rate laws and theoretical concepts pertinent to kinetics appears in the literature (Aagaard and Helgeson, 1982; Cassford et al., 1983; Helgeson et al., 1984; Holdren and Berner, 1979; Lasaga, 1981a,b, 1984; Morse, 1983; Nancollas, 1979; Nancollas and Tomson, 1976; Nielsen, 1964; Petrovich, 1976, 1981a,b; Plummer et al., 1979; and Wolery, 1986b). The more significant and widely used of these are discussed here.

Although progress has been made recently in the field of geochemical kinetics, there is still considerable controversy regarding rate-law forms. All users of the EQ6 kinetics capability should have some understanding of the current literature because EQ6 is constructed to make the user responsible for some critical decisions, such as the actual form of the rate law to use and the necessary constants. The development of the EQ6 kinetics capability has been useful in testing kinetics theories.

In this section we briefly review existing rate equations, taking into account two important considerations. First, the same mathematical form of a rate law may arise from very different mechanistic assumptions. Therefore, the fact that a particular set of data can be fit to a particular rate law is not usually sufficient to prove the validity of the corresponding assumed mechanism. Second, the rate law that follows a given set of physical assumptions may be expressed by more than one mathematical form.

The literature employs various systems of notation for dissolution/precipitation kinetics. To present a coherent discussion, we have chosen to use notation consistent with the documentation provided by Wolery (1986b). As a result, we have had to alter the notation from that used in the cited sources in two instances. Analogs of these equations can be created by substituting one type of concentration for another. For example, molal (m) or molar (c) concentration may be replaced, respectively, by total molal (m^T) or molar concentration (c^T). The substitution of molal concentration for molar concentration requires that Ω, the mass (kg) of solvent water, be substituted for V_s, the solution volume. Such substitutions result in changes that are assumed to control the kinetics, which gives rise to corresponding differences in the definitions of the rate parameters. Usually, these changes are numerically negligible.

3.1. Simple Rate Laws in m^{eq}

Precipitation rates for crystal growth controlled by interface processes or by bulk diffusion of ions to the crystal surface have been described by equations of the form

$$-dm_i^T/dt = \left(\frac{s}{\Omega}\right) k_- \left(m_i - m_i^{eq}\right)^n \quad , \tag{3-1}$$

where m^T is the total molal concentration (free ion plus complexes) of some constituent ion i in the solid, s is the surface area available for crystal growth, k_- is the rate constant for precipitation, m_i is the free (uncomplexed) molal concentration, m_i^{eq} is the value of m_i at equilibrium, and n is a constant (unity in the case of diffusion models). This form can also be used to describe dissolution. The molal form is given here because it appears in the literature more frequently. Several rate-law equations that can be related to Eq. 3-1 have been reported (cf. Bochner et al., 1984; Liu et al., 1976; Liu and Nancollas, 1970; Nancollas, 1979; and Nancollas and Tomson, 1976). For equations of this type, m^{eq} can usually be regarded, at least conceptually, as a substitute for the equilibrium constant of the corresponding reaction.

Equation 3-1 and analogous expressions have long been favored in the literature because they provide a compact means of representing experimental results obtained using relatively simple laboratory procedures. A drawback to using this rate-law form is the ambiguity in the "equilibrium concentration" parameter. If more than one aqueous solute species participates in the formation of the solid, the equilibrium concentration is not a constant for any of the species. The law of mass action requires the equilibrium concentration to be a function of the composition of the solution. For example, if the dissolution rate of NaCl is described by changes in the concentration of Na$^+$, then m^{eq} has a unique value only in pure saturated NaCl solution. If the system is expanded to NaCl-KCl-H$_2$O, then m^{eq} is also a function of how much KCl is present.

The following equation (somewhat analogous to Eq. 3-1) has been used to describe mineral precipitation for solutions composed of such aqueous electrolyte mixtures (cf. Liu and Nancollas, 1970; Reddy, 1977; Nancollas et al., 1979; and Reddy and Wang, 1980):

$$dm_s/dt = \left(\frac{s}{\Omega}\right) k_- \left(m_s^{eq} - m_s\right)^n \quad . \tag{3-2}$$

The subscript s denotes the precipitating solid instead of a constituent ion, m_s is the number of moles of solid per kilogram of solution, and m_s^{eq} is the value of m_s at equilibrium. Equations of this form are useful in fitting experimental rate measurements, although m_s^{eq} in this equation is much farther removed from the equilibrium constant than is the m^{eq} in Eq. 3-1.

Equations 3-1 and 3-2 are of limited usefulness for modeling systems other than those from which the corresponding data were generated. Recently, the fit of this equation form to experimental data for calcite precipitation has been challenged (Reddy et al., 1981). Experimental data that are reported and subsequently interpreted using this form can be reevaluated using a more general rate-law form. For example, in Eq. 3-1, when $n = 1$ and i is a nonionic species, this rate law closely resembles the mathematical form of the transition-state theory (TST) rate law discussed in Section 3.3. Thus, no equations of the type represented by Eqs. 3-1 and 3-2 have been programmed into EQ6.

3.2. Activity-Term Rate Laws

Some authors have interpreted kinetic experimental data as a complex mixture of dissolution and precipitation processes. The mechanism is represented as the sum of several reactions occuring simultaneously on the surface of the solid. A net rate equation is obtained by the summation of individual terms, each containing a rate constant (k_i) and an activity product. This type of rate-law form can be represented by

$$v_j = s \sum_i k_i \prod_k a_k^{n_{ik}} \quad . \tag{3-3}$$

Although rate equations of the above form have been derived principally to describe the results of dissolution-rate experiments, they can also be used to describe precipitation rates. If the rate constants are constrained to satisfy the condition of zero rate at equilibrium (i.e., to be consistent with the value of the equilibrium constant), the same equation can be used to describe reaction rates in both the forward and backward directions. This allows the precipitation rates to be obtained from dissolution data.

Plummer et al. (1978) used an example of this rate-law form to describe the dissolution data of calcite:

$$v_j = s \left(k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} \right.$$

$$\left. + k_4 a_{Ca^{2+}} a_{HCO_3^-} \right) \quad . \tag{3-4}$$

To be consistent with Eq. 3-3, k_4 has to be cast as a positive quantity. Thermodynamic consistency requires that

$$-k_4 = \frac{K_2}{K_{sp}} \left[k_1 + \frac{1}{a_{H^+}} \left(k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} \right) \right] \quad . \tag{3-5}$$

Thus, k_4 is dependent on solution composition and not an actual constant. Plummer et al. (1978) fit Eq. 3-4, as a four-constant rate law, to experimental data for a limited range of solution composition. They found good agreement with the value obtained for k_4 when compared with the value calculated from Eq. 3-5. Good results were also obtained for both calcite dissolution and precipitation (cf. House, 1981; Reddy et al., 1981; and Cassford et al., 1983). Eary and Cathles (1983) have used a similar equation to describe the kinetics of uranium (VI) peroxide hydrate precipitation.

The general form of this rate law, represented by Eq. 3-4, has been programmed into EQ6. Its functional form does not have the problems associated with those represented by Eqs. 3-1 or 3-2. Also, it seems to work well for describing the dissolution and precipitation kinetics of calcite, an important phase in aqueous geochemistry. Although Plummer et al. (1978) attach theoretical significance to each of the four terms in their model for calcite, different theoretical assumptions appear to be equally capable of explaining the observable data (see Section 6.2).

3.3. Transition-State Theory

Rate equations employing TST have a strong basis in theory and are receiving increasing attention in geochemistry (cf. Rimstidt and Barnes, 1980; Aagaard and Helgeson, 1982; Helgeson and Murphy, 1983; Lasaga, 1981a,b; Helgeson et al., 1984; Wolery, 1986b; Knauss and Wolery, 1986). This theory of reaction rates requires that there be a corresponding microscopic (or elementary) reaction for every macroscopic reaction.

A pair of macroscopic and microscopic reactions follows the general format (Wolery, 1986b):

$$(-j) \text{ [mineral]} + \text{ other reactants}$$
$$= \text{ products (macroscopic)} \tag{3-6}$$

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and

$(-i)$ [mineral] + other reactants + catalysts
$= 1$ [activated complex]* = products
+ catalysts (microscopic) . (3-7)
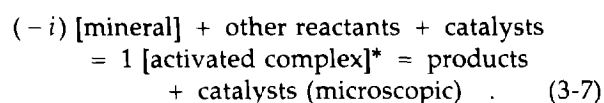
Equation 3-6 follows the format of a reaction as stored on the EQ3/6 thermodynamic database. The coefficient j is usually unity, and the stoichiometric coefficient of the activated complex is always unity.

A microscopic reaction differs from its macroscopic counterpart in three distinct ways. First, instead of just reactants on the left and products on the right, the activated complex appears in the middle. Second, certain additional reactant species that are regenerated as products may appear. These species may be informally termed "catalysts." Third, a stoichiometric nonequivalence may exist between the macroscopic and microscopic reactions.

The stoichiometric equivalence of Eqs. 3-6 and 3-7 is usually treated through one of the following two parameters:

$$\sigma = j/i \qquad (3\text{-}8)$$

and

$$m = i/j \, (\, = 1/\sigma) \ . \qquad (3\text{-}9)$$

The parameter σ is favored by Helgeson and coworkers (cf. Aagaard and Helgeson, 1982; Helgeson and Murphy, 1983; and Helgeson et al., 1984). Lasaga (1984) prefers to use the parameter m. Wolery (1986b) presents a detailed derivation of the rate equations in which these parameters appear.

An example of macroscopic and microscopic reactions are given for pure silica phase $SiO_2(s)$, which could be quartz, cristobalite, etc. The reactions below are an adaptation of the model presented or suggested by Rimstidt and Barnes (1980). The macroscopic reaction may be written as

$$SiO_2(s) = SiO_2^\circ \ , \qquad (3\text{-}10)$$

where SiO_2° is the species dissolved silica. If water is assumed to promote this process, the corresponding microscopic reaction can be written as

$$SiO_2(s) + n \, H_2O \, (l) = \left[SiO_2 \cdot nH_2O\right]^*$$

$$= SiO_2^\circ + n \, H_2O \, (l) \quad . \qquad (3\text{-}11)$$

No particular value of n is suggested here, although it must be a positive number.

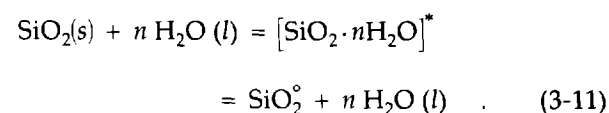The rate equations for TST can be developed from more than one set of physical assumptions (Wolery, 1986b). The development that is usually presented in the literature (e.g., Rimstidt and Barnes, 1980; Aagaard and Helgeson, 1982; Lasaga, 1981a,b), and called TST-A1 by Wolery (1986b), contains a logical inconsistency that requires one to assume simultaneous equilibrium of the activated complex with both reactants and products. This inconsistency has been pointed out most recently by Lasaga (1981b). In his view, the equations must, therefore, be considered representative of extrapolation of the rate about the point of thermodynamic equilibrium. Wolery (1986b) presents an alternative development called NESS-TST (Non-Equilibrium Steady-State Transition-State Theory), which is based on a steady-state assumption, rather than on one of simultaneous equilibria. This development leads to a set of practical rate equations that are essentially the same. Although there are some minor differences, they are not significant when the TST equations are run in the EQ6 code.

The net rate equations for macroscopic reactions that have been incorporated into EQ6 are:

$$v_j = s \, k_+ \, q_+ \left[1 - \exp\left(A_+/\sigma RT\right)\right] \qquad (3\text{-}12)$$

and

$$-v_j = s \, k_- \, q_- \left[1 - \exp\left(A_-/\sigma RT\right)\right] \quad . \qquad (3\text{-}13)$$

Equation 3-12 is an expression for the net rate in the forward direction and is written in terms of forward direction parameters. Equation 3-13 is the backward direction analog. Although Eqs. 3-12 and 3-13 are strictly equivalent under the assumptions of the theory, both forms have been programmed into the EQ6 code primarily for convenience. Having both forms available allows the user some flexibility in inputting rate parameters. While it also permits the use of an inconsistent pair of equations, one to describe the net rate when it is in the forward direction and another when it is in the reverse direction, such use is not recommended. The relationships required for strict consistency will be discussed in the next paragraphs.

All of the parameters in Eqs. 3-12 and 3-13 have been introduced previously, except for q_+ and q_-, which are defined as "kinetic activity

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products." The simple activity products for the left side of the microscopic reaction are

$$q_+ = a_s a_w^n \quad , \tag{3-14}$$

where a_s is the activity of the solid and a_w is the activity of water.

The kinetic activity products are related to the activity product of the macroscopic reaction (Wolery, 1986b) by

$$Q_+^m = \frac{q_-}{q_+} \quad . \tag{3-15}$$

A similar relationship holds for the rate constants and the equilibrium constant for the macroscopic reaction.

$$K_+^m = \frac{k_+}{k_-} \quad . \tag{3-16}$$

This important relationship suggests that precipitation rate constants, which are often difficult to measure because of the precipitation of unwanted phases, can be estimated from dissolution rate constants and equilibrium constants. However, this can only be done if m (or, equivalently, σ) is known (Wolery, 1986b). Equation 3-16 is sometimes given in the literature without the m exponent, corresponding to the case equivalent of $m = 1$.

The following forms of the equations are, according to the theory, strictly equivalent to Eqs. 3-12 and 3-13. They have not been programmed into the code, but are given here to help readers recognize equivalent forms when they encounter them in the literature. They include

$$v_j = s \left(k_+ q_+ - k_- q_- \right) \quad , \tag{3-17}$$

$$v_j = s k_+ q_+ \left[1 - (Q_+/K_+)^m \right] \quad , \tag{3-18}$$

and

$$- v_j = s k_- q_- \left[1 - (Q_-/K_-)^m \right] \quad , \tag{3-19}$$

where s represents surface area.

Some important limiting relationships can be associated with the TST net rate law (cf. Lasaga, 1981a,b; Aagaard and Helgeson, 1982; Helgeson et al., 1984; Wolery, 1986b). Far from equilibrium in the direction of undersaturation, the rate of a reaction, v_j, can be expressed as

$$v_j = s k_+ q_+ \quad . \tag{3-20}$$

The accompanying reaction rate far from equilibrium in the direction of supersaturation is

$$- v_j = s k_- q_- \quad . \tag{3-21}$$

Note that the rates of dissolution and precipitation far from equilibrium are independent of m (or σ). Near equilibrium, however, the rate becomes proportional to the thermodynamic affinity and depends on m or σ (Aagaard and Helgeson, 1982; Helgeson et al., 1984). The net rate equations for both the forward and backward directions predict zero reaction rates at equilibrium:

$$v_j \simeq s k_+ q_+ \left(\frac{A_+}{\sigma RT} \right) \tag{3-22}$$

and

$$- v_j \simeq s k_- q_- \left(\frac{A_-}{\sigma RT} \right) \quad . \tag{3-23}$$

Still other forms of the TST equations are possible (Wolery, 1986b), although some require special assumptions. These forms are useful in comparing equations that appear in the kinetics literature. One approach is to factor the kinetic activity products into corresponding concentration and activity coefficient parts. For q_+, this is illustrated by

$$q_+ = m_+ \gamma_+ \tag{3-24}$$

(q_- is treated analogously). This is straightforward so long as the species involved in the products are aqueous solutes. For other species whose activities cannot be factored into molal concentrations and molal activity coefficients, a simple approach is to factor their activities in q_+ (or q_-) into m_+ (or m_-). Parallel factoring of the activity product of the macroscopic reaction gives

$$Q_+ = M_+ \Gamma_+ \quad . \tag{3-25}$$

(Q_- can be factored analogously.) It follows that

$$M_+^m = \frac{m_-}{m_+} \tag{3-26}$$

and

$$\Gamma_+^m = \frac{\gamma_-}{\gamma_+} \quad . \tag{3-27}$$

The apparent equilibrium constant for the forward direction can be defined as

$$K'_+ = \frac{K_+}{\Gamma_+} \quad . \tag{3-28}$$

It can be shown that Eqs. 3-18 and 3-19 can be recast in the following forms:

$$v_j = s\,k_+\,\gamma_+\,m_+\left[1 - \left(M_+/K'_+\right)^m\right] \tag{3-29}$$

and

$$-v_j = s\,k_-\,\gamma_-\,m_-\left[1 - \left(M_-/K'_-\right)^m\right] \quad . \tag{3-30}$$

Forms related to these equations appear in the literature, often with no derivation or citation of any theoretical origin (e.g., Marshall and Nancollas, 1969; Reddy and Nancollas, 1971; Wiechers et al., 1975). For example, Reddy and Nancollas (1971) give an equation of the form

$$dm_i^T/dt = -s\,k_p\left[M_+ - \left(K_+/\Gamma_+\right)\right] \tag{3-31}$$

for the case of calcite growth kinetics. Here, k_p is a precipitation rate constant, which we choose to distinguish from k_-. The corresponding reaction, written in dissolution form according to our convention, is

$$CaCO_3(s) = Ca^{2+} + CO_3^{2-} \quad . \tag{3-32}$$
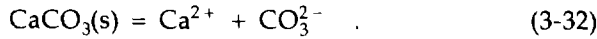
If a factor of w_w is considered to be in the denominator on the right side of Eq. 3-31, this equation can be transformed to

$$-v_j = s\,k_p\,M_+\left[1 - \left(M_-/K'_-\right)\right] \quad . \tag{3-33}$$

If we take the microscopic analog of the reaction, Eq. 3-32, to be

$$CaCO_3(s) = \left[CaCO_3\right]^* = Ca^{2+} + CO_3^{2-} \quad , \tag{3-34}$$
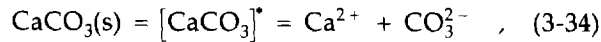
Eq. 3-30, the TST equation, becomes equivalent to Eq. 3-33, except that a factor of $(k_p\,M_+)$ appears in the latter instead of $(k_-\,q_-)$. Note that Eqs. 3-32 and 3-34 require $m = 1$. In this particular microscopic reaction, there are no aqueous species among the reactants and no catalysts. Hence, M_+ reduces to m_-. It is possible to consider the activity coefficient factor γ_- as implicitly present in the rate constant in Eq. 3-31; that is, to assume that $k_p = k_-\,\gamma_-$. Then, in this particular case, Eq. 3-31 is equivalent to the TST expression, Eq. 3-30. The

general form of Eq. 3-31, however, is not consistent with transition-state theory. Still other rate law forms exist for describing the dissolution and precipitation kinetics of calcite and resemble TST equations to some degree (e.g., Sjöberg, 1976; Cassford et al., 1983; House, 1981; and Morse, 1983).

It is of some interest, however, to look at the TST rate law for silica dissolution/precipitation by Rimstidt and Barnes (1980). They give the following equation to describe rates in dilute solutions of dissolved silica:

$$da_{H_4SiO_4^\circ}/dt = \left(\frac{s}{w_w}\right)\left(\gamma_{H_4SiO_4^\circ}\right)$$
$$\left(k_+\,a_{SiO_2(s)}\,a_{H_2O(l)}^2 - k_-\,a_{H_4SiO_4^\circ}\right) \quad . \tag{3-35}$$

This corresponds to the macroscopic dissolution equation

$$SiO_2(s) + 2\,H_2O(l) = H_4SiO_4^\circ \quad . \tag{3-36}$$
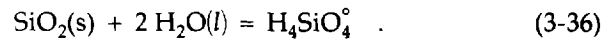
Rimstidt and Barnes (1980) present the rate in terms of rate of change in activity rather than rate of change in concentration. They also use a formally the hydrated species to represent aqueous silica. In their derivation, the activity coefficient of aqueous silica is assumed to be constant. (For the stated set of conditions, it should be close to unity). Recasting their equation gives

$$v_j = s\left(k_+\,a_s\,a_w^2 - k_-\,a_{H_4SiO_4^\circ}\right) \quad , \tag{3-37}$$

which is a form of Eq. 3-17. The corresponding microscopic equation is

$$SiO_2(s) + 2\,H_2O(l) = \left[SiO_2\cdot2H_2O\right]^*$$
$$= H_4SiO_4^\circ \quad . \tag{3-38}$$
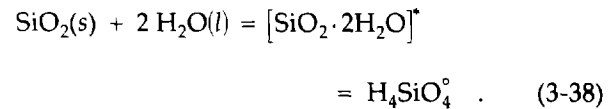
Note that the water is not catalytic because it is not regenerated as a product. The model represented by reactions in Eqs. 3-36 and 3-38 is equivalent to that given earlier by Eqs. 3-10 and 3-11 (with n in Eq. 3-11 set to zero), where aqueous silica was represented as the anhydrous species. The formal degree of hydration one chooses for aqueous species does not affect the TST rate equations as long as one is consistent (Wolery, 1986b). Thus, one may use the Rimstidt and Barnes (1980) rate constants for equations corresponding to reactions in Eqs. 3-10 and 3-11.

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The Rimstidt and Barnes (1980) rate law can be reduced to m^{eq} form if one assumes that γ for aqueous silica is numerically constant. If the hydrated form of aqueous silica is used, one must also assume that the activity of water is unity. Both of these assumptions tend to hold well under the conditions for which the rate law is stated to be valid. Thus, $Q_- = 1/(m\gamma)$, $q_- = m\gamma$, $m^{eq} = 1/(K_-\gamma)$, and the rate law can be written as

$$-dm/dt = \left(\frac{s}{w_w}\right) k_- \gamma (m - m^{eq}) \quad . \tag{3-39}$$

If it is further assumed that $\gamma = 1$, this Eq. 3-39 is analogous to Eq. 3-1.

3.4. Temperature and Pressure Dependence of Rate Constants

The temperature dependence of a rate constant is commonly described by an activation energy, E_a:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad . \tag{3-40}$$

If this equation is integrated treating E_a as a constant, then

$$\ln k_{T_2} = \ln k_{T_1} + \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \tag{3-41}$$

For TST, the forward and backward activation energies are related by the equation

$$E_{a,+} - E_{a,-} = m \Delta H^\circ_{r,+} \quad , \tag{3-42}$$

where $\Delta H^\circ_{r,+}$ is the standard partial molal enthalpy of reaction for the macroscopic reaction (for the forward direction) and m is a stiochiometric factor (see Wolery, 1986b). Thus, in principle, activation energies for precipitation can be estimated from activation energies for dissolution.

In TST, the temperature dependence of the rate constant, k, can also be related to the enthalpy of formation of the activated complex, H_a. The governing equation is

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{H_a}{RT^2} \quad . \tag{3-43}$$

If the enthalpy of activation is treated as a constant, the integration of this equation yields

$$\ln k_{T_2} = \ln k_{T_1} + \ln (T_2/T_1)$$

$$+ \frac{H_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \tag{3-44}$$

The activation enthalpies for the forward and reverse directions are related to each other by

$$H_{a,+} - H_{a,-} = m \Delta H^\circ_{r,+} \quad . \tag{3-45}$$

Corresponding activation energies and enthalpies are related by

$$E_a = H_a + RT \quad . \tag{3-46}$$

The temperature dependence of a reaction may be approximated by assuming that either the activation energy or the activation enthalpy is constant. However, these assumptions are not mutually exclusive because of the RT factor in Eq. 3-46.

The pressure dependence of rate constants can be treated in an analogous manner. The governing equation from thermodynamics is

$$\frac{d \ln k}{dP} = -\frac{V_a}{RT} \quad . \tag{3-47}$$

Here V_a is the activation volume. If this equation is integrated treating the activation volume as a constant, then

$$\ln k_{P_2} = \ln k_{P_1} - \frac{V_a}{RT}(P_2 - P_1) \quad . \tag{3-48}$$

The forward and backward volumes of activation are related to each other by the standard partial molal volume of reaction,

$$V_{a,+} - V_{a,-} = m \Delta V^\circ_{r,+} \quad . \tag{3-49}$$

These relationships may help users of the EQ6 kinetics capability estimate necessary rate data. For a more complete derivation of temperature and pressure rate-constant relationships, see Appendix D of Wolery (1986b). At present, temperature correction is built into the EQ6 code by means of constant activation energy calculations according to Eq. 3-41. A rate-constant-activation-energy pair must be given on the input file along with the corresponding temperature, which need not be the actual temperature for the run. The actual temperature for the run may, itself, change during the run. To date, no pressure corrections have been built into the code.

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3.5. Surface Area Considerations

The dissolution and precipitation rates for minerals and other solids depend on the active surface area available for the reaction process. Surface area measurements are usually made using BET gas absorption techniques on bulk samples (e.g., Brandse et al., 1977; Liu et al., 1976; House, 1981; Reddy et al., 1981; and Rimstidt and Barnes, 1980). Another technique for estimating surface areas is to use the sample weight (referred to as the "charge" in dissolution experiments or "seed material" in precipitation experiments) as proportional to the surface area (e.g., Marshall and Nancollas, 1969; Liu and Nancollas, 1970; Reddy and Nancollas, 1971; Reddy and Wang, 1980; Reddy, 1977; Wiechers et al., 1975; and Lagache, 1965, 1976). If surface area has not been measured, it is also possible to estimate a value geometrically if the samples have been prepared in a narrow size range. The specific surface area ($s_\#$) is area per unit mass and is usually expressed in units of square centimeters per gram. If a particle is assumed to be spherical, the specific surface area can be calculated from

$$s_\# = \frac{6}{\rho D} \quad , \tag{3-50}$$

where D is diameter and ρ is grain density (assuming no porosity). If the particle shape is assumed to be cubic,

$$s_\# = \frac{6}{\rho a} \quad , \tag{3-51}$$

where a is the edge length. Sometimes a shape factor that has a value typically in the range of 2 to 3 is added to the right side of these equations.

It is important for the treatment of rate constants and surface areas to be consistent. This is because only the product of rate constant and surface area can actually be "measured" in rate experiments. Surface area estimation techniques have been found to yield inconsistent results for the same sample. Thus, if a rate constant is inferred from a BET measurement, it is probably best used in rate equations with surface area estimates based on the same technique.

EQ6 allows the user to consider a kinetically effective surface area as smaller than the actual surface area. Models of this type are described by using the variable FK on the input file that represents the kinetically active fraction of the total surface area.

Helgeson et al. (1984) propose to restrict the active surface area of a phase such as a feldspar to the relatively small area composed of etch pits. These pits are the locus of most of the actual dissolution that appears to take place in the laboratory (cf. Holdren and Berner, 1979; Knauss and Wolery, 1986) and in field observation (Berner and Holdren, 1979). Whether the surface area is most properly treated by this approach remains to be seen. The relevance of having an active surface area that corresponds to specific sites associated with precipitation processes also remains to be identified. Although feldspar dissolution is clearly dominated by etch-pit formation, SEM photographs of the growth surfaces of feldspars reveal no corresponding features (cf. Ali and Turner, 1982).

An additional factor to consider is the possibility of syntactic growth in which a grain of one mineral serves as a seed for a crystallographically similar mineral (e.g., calcite growth on dolomite or celestite growth on barite). Syntatic growth represents a type of coupling that has not received much attention in precipitation kinetics studies, but might be important to certain modeling scenarios. At present, there is no treatment of growth kinetics in EQ6.

The increase in surface area during crystal growth has been taken into account in some precipitation studies (e.g., Marshall and Nancollas, 1969; Brandse et al., 1977). This correction may not be necessary, however, if the amount of precipitated material is small compared to the amount of seed crystals. Surface areas of crystals have been observed to increase as a result of dissolution if the increase in specific surface area outstrips the dissolution of material (Grandstaff, 1978).

Two options presently exist for the treatment of surface area in EQ6. Either the total surface area is constant, which ignores all corrections due to growth or dissolution, or the specific surface area (ratio of the area/unit mass) is constant. Additional considerations on growing of particles, based on equations such as 3-51 or 3-52, may be added in the future. Note, in the case of growth kinetics, these equations imply that specific surface area decreases with time. Thus, this assumption may lead one to overestimate the actual surface area.

A final point concerns the estimation of surface area for individual minerals in a rock sample. A BET measurement can only give the surface area of a sample as a whole. In the absence of other information, the best procedure is probably to apportion the measured surface area according to the volume percentages of the minerals in the rock.

3.6. Other Considerations

The rate equations discussed earlier in this section apply only to the case of homogeneously dissolving or precipitating material. Such homogeneity is not always achieved in sample preparation procedures for dissolution experiments or for seeded precipitation experiments. Inhomogeneity results when material in a sample is "disturbed" (i.e., is strained and/or exists as very fine particles below a critical size limit). This "disturbed" material is thermodynamically less stable than the undisturbed material of the same composition (cf. Holdren and Berner, 1979).

The effect of submicron particles clinging to larger grains in dissolution experiments on feldspars was documented by Holdren and Berner (1979). They used SEM to establish the existence of an "ultrafine" component and showed, by means of washing and etching the surface, that elevated dissolution rates in the early stage of an experiment were due to the presence of this component. Recognition of the enhanced dissolution effect in geochemistry stems largely from Holdren and Berner's work. However, earlier studies of the dissolution of quartz noted similar findings (see sources cited by Petrovich, 1981a; also see Beckwith and Reeve, 1969).

The HF etching procedure used by Holdren and Berner (1979) is no longer recommended (cf. Perry et al., 1983). Instead, the ultrafine component can be best removed by washing the sample ultrasonically and decanting the solution (cf. Neil and Apps, 1980; Knauss and Wolery, 1986) This process does not remove all of the "disturbed" material, such as around strained surfaces or on sharp corners of larger grains. The effect of "disturbed material" on precipitation processes has not been evaluated and may require explicit recognition in the analysis of an experiment of a recrystallization effect. Because of its lesser thermodynamic stability, such material may be dissolving even though the solution is supersaturated relative to a more stable bulk material.

The thermodynamic properties and/or kinetic rate constants related to the nature and properties of "disturbed" material that may adhere to the surface of a phase may vary. If the presence of such material causes the thermodynamic properties to vary, with or without corresponding variations in the rate constants, EQ3/6 would have to add one or more "disturbed material" components for each mineral being treated. At present, no options are available to assist with such a treatment. The "disturbed" components of a mineral would have to be added to the thermodynamic database as "new" minerals.

Another caveat concerning the rate-laws discussed in this section is that they do not account explicitly for speciation on the surfaces of dissolving and growing minerals. A future direction for rate studies in aqueous geochemical systems would be the development of dissolution and precipitation rate-laws that are coupled to models of surface speciation. There are several reasons to expect such a development. One is that the stoichiometric coefficients of catalysts such as H^+ in TST rate laws often appear to be fractional values (cf. Lasaga, 1981a, 1984; Helgeson et al., 1984; and Knauss and Wolery, 1986). This suggests that the actual catalyst in such a case is a corresponding surface species. Lasaga (1981a) gives a simple model for a feldspar dissolution rate that is coupled with sorption of H^+ on the mineral surface. This model appears to explain the observed fractional dependency. At present, EQ6 does not have a capability for treating mineral surfaces.

Rate-law forms often vary with environmental parameters, such as pH or temperature. For example, the dissolution of feldspar appears to require three TST rate laws to explain observations across the range of pH values in the range 25 to 70°C (Helgson et al., 1984; Knauss and Wolery, 1986). In each proposed mechanism, H^+ plays a different role as catalyst. At low, intermediate, and high pH, the catalyst is H^+, none, and OH^-, respectively. To account for these types of kinetic models, we have chosen to treat EQ6 rates as a sum of rates predicted by up to four individual mechanisms. This allows code calculations crossing apparent rate-law boundaries to be made. For example, it allows the reproduction of feldspar dissolution rate data across the total pH range.

4. EQ6 Code Modifications

A number of modifications have been made to the EQ6 code as a result of extending the kinetics option to include precipitation as well as dissolution. These changes were made in developing the 3245 version of EQ6 from the previous 3230B version. This section describes the changes.

In the 3230B version, the kinetics option (IOPT1 = 1) allows rate-law specifications to be

made for mineral dissolution only. A dissolving mineral follows the specified rate law as long as the dissolution affinity (A_+) remains positive. Dissolution ceases if the mineral becomes exhausted. If the phase boundary (point of overall reaction progress at which equilibrium is reached) occurs in finite time, the boundary is actually overstepped by a small amount until some of the mineral reprecipitates as an equilibrium phase. The phase boundary search routine actually uses a target affinity corresponding to a small negative value of A_+. The actual equilibrium phase precipitation may be further delayed until a sufficiently well-conditioned Jacobian matrix, necessary to accomplish the precipitation, is attained. Once this happens, any mass of the mineral that remains as a reactant is transferred to the mass in the equilibrium system. Any subsequent dissolution or precipitation is controlled by maintaining solubility equilibrium.

The coding changes required to include kinetically governed precipitation fall into several categories. Among them are additional input/output, new coding for evaluating precipitation rate laws, changes to prevent instantaneous equilibrium precipitation of supersaturated phases, and new routines to deal with approaching phase boundaries from supersaturation. Details of these changes follow.

Phases whose dissolution and/or precipitation are to be controlled by kinetics are termed "reactants." These phases and the data required to evaluate their corresponding rate laws are defined on the EQ6 INPUT file. Specifications for precipitation kinetics were added to the INPUT file, paralleling the previous specifications for dissolution kinetics. When the aqueous solution starts to become supersaturated with a solid phase, the default response of the EQ6 code is to precipitate that phase according to instantaneous solubility equilibrium. EQ6 now recognizes all solid phases listed as "reactants" on the INPUT file, including those for which the precipitation kinetics option is specified, as belonging to a special class of minerals.

Separate rate expressions can be specified for net dissolution and net precipitation. The code checks the thermodynamic affinity (A_+) to determine which expression to use (rate evaluations are made in subroutine RTCALC). A single rate law describing net mass transfer in both directions can be used for rate laws that are consistent with thermodynamics, i.e., that predict mass transfer in the direction consistent with thermodynamic driving force. They include the affinity-term rate-laws

and transition-state theory rate expressions. The code avoids possible violations of thermodynamic constraints by setting rates to zero in the absence of a favorable thermodynamic driving force.

All kinetic data for "reactants" are read from a new subroutine READRT, which is called from subroutine READZ (the principal routine for reading the INPUT file). Surface area, rate-law code, and the rate-law constants for each "reactant" are read from the INPUT file. The rate-law code identifies a corresponding rate-law that has been programmed into subroutine RTCALC. Separate rate-law codes for dissolution and precipitation, embodied in the parameters NRK and NRPK, have been provided for user convenience.

Dissolution NRK flags have been changed from the 3230 version, and precipitation flags, NRKP have been added. The current usage of these parameters is discussed in the following section. The affinity-term rate law form has been added as a new option for both dissolution and precipitation. The transition-state theory rate law (activated when NRK = 2) has been changed to increase the maximum number of parallel rate-law mechanisms from three to four. This change has necessitated the redimensioning of some arrays in COMMON BLOCK /RK/.

A new COMMON BLOCK, /RPK/, was created to contain the precipitation rate input variables (which paralleled the existing ones for the dissolution rate) and two flag arrays (NMCHK, NXCHK) that indicate whether a mineral or solid-solution end member is specified in the INPUT file as a reactant with precipitation kinetics. These flags are used later in subroutines PATH, SATCHK, and SCRIPZ. In PATH, when such a mineral (or solid solution) is supersaturated, a flag is set to control the affinity value; this value is the target of the phase boundary search, which calculates an upper limit on step size. In subroutine SATCHK, the flags are used to discriminate supersaturated minerals that are to precipitate kinetically from those that are to be precipitated instantaneously to satisfy solubility equilibrium. In subroutine SCRIPZ, these flags are used in constructing some tables written on the OUTPUT file.

Many format statements had to be inserted and/or changed in several subroutines to include the added kinetic information on the OUTPUT and PICKUP files. Subroutine ECHOZ was modified to print out the rate-law codes and rate coefficients for each "reactant" specified on the INPUT file. Subroutine SCRIBE, which writes the PICKUP file, was modified to include the rate data for precipitation kinetics. Subroutine

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SCRIPZ, which writes a description of the state of the system at selected points of reaction progress, was modified to print a more complete description of reaction rates and reactant amounts. Several changes have been made to the summary OUTPUT tables (TAB files).

If specified rate laws for both dissolution and precipitation are selected, the phase is never formed as an equilibrium phase. In this case, the step size must be controlled during the run so that a rate function is never extrapolated across the phase boundary. The search for the phase boundary targets the true boundary ($A_- = 0$). The step size is then restricted such that a point of reaction progress falls on the boundary (within a tolerance interval based on the difference between the affinity and zero), thereby avoiding what could be improper extrapolation.

EQ6 currently does not allow a rate law to be input for precipitation of a reactant unless one is also provided for dissolution. If such input is attempted, an error message is issued, followed by termination of execution. Logically, one might hope to treat such a condition in a manner similar to that when a dissolution rate law is input without a precipitation rate law, that is, to convert the reactant mass to equilibrium mineral form upon reaching the phase boundary or some nearby target point and to treat subsequent dissolution or precipitation according to instantaneous solubility equilibrium.

The problem with this approach is that one can not guarantee that enough "reactant" mass will always be present to generate a sufficiently well-conditioned Jacobian matrix with the mineral in the system as an equilibrium phase. In essence, this problem results because of finite length numbers being stored on digital computers. The problem can be avoided in the opposite case (where dissolution rate is specified without a precipitation rate) by moving across the phase boundary to some point where a stable Jacobian results (such a point is either found or the "reactant" mass exhausts at some degree of supersaturation). For precipitation only, no comparably satisfactory parallel technique exists.

5. EQ6 Rate Law Options

To use the precipitation kinetics option, the user must specify IOPT1 = 1 (kinetics option) on the INPUT file. This option is required to run EQ6 with any kinetic rate laws. If IOPT1 = 0, the rate laws specified for all reactants must be of the relative rate type, where the resulting rate calculations have no time framework. If the user desires, relative rate specified reactants and actual kinetic rate specified reactants can be mixed in a single run if at least one kinetic rate reactant is specified and IOPT1 = 1.

A rate law must be specified for each reactant and entered on the INPUT file. The rate laws, themselves, are specified by the rate-law codes NRK and NRPK, which pertain to net dissolution and precipitation, respectively. The following tables summarize the rate-law options currently programmed:

NRK Values	Dissolution Rate Law
0	Illegal value
1	Relative rate law
2	Transition-state theory rate law
3	Linear plus parabolic rate law
4	Activity-term rate law

NRPK Values	Precipitation Rate Law
-1	Use the dissolution rate input (NRK must be 2 or 4)
0	Precipitation governed by instantaneous equilibrium
1	Relative rate law
2	Transition-state theory rate law
3	Linear (constant) rate law
4	Activity-term rate law

The affinity to precipitate (A_-) is used in the code as the principal variable for determining thermodynamic driving force for nonequilibrium reactions. EQ6 checks this affinity for each reactant before calculating its corresponding rate. If the affinity is zero (reaction equilibrium), the code sets the rate to zero (the rate expressions specified on the INPUT file are not evaluated). If A_- is negative (implying that A_+ is positive), the rate expression specified for dissolution is evaluated. The value of the rate must be positive to be consistent with dissolution. If the expression is negative (i.e., the expression predicts precipitation), the rate is set to zero. If A_- is positive, the rate expression for precipitation is evaluated. The calculated rate

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must be a negative value to be consistent with precipitation; if it is not, the rate will be set to zero.

A "special" reactant (one whose composition is defined on the INPUT file, identified by JCODE = 2; see Wolery, 1986a), as currently treated, has no thermodynamic stability and will never precipitate. The "special" reactant capability was intended primarily to allow the definition of a reactant that corresponds to a bulk rock composition, not as a substitute for entering phases in the thermodynamic database. The use of "special" reactants in actual kinetic calculations should be avoided in most instances.

In the sections that follow, the equations programmed into the EQ6 code for each of the precipitation rate laws specified by the input variable NRPK are reproduced using the code variables. The companion equations for the dissolution rate laws specified by the input variable NRK are listed in the *EQ6 User's Manual* (Wolery, 1986a) and are not reproduced here. Reactants are indexed by the parameter NRC, which runs from 1 to NRCT, the total number of reactants.

5.1. Currently Programmed Precipitation Rate Laws

5.1.1. Relative Rate Law

A phase may be precipitated using the relative rate law when the amount precipitated is not a function of time, but of the overall reaction progress variable. This may be desirable when no experimental kinetic data are available for a system (see Section 3.3 in Wolery, 1986a). The relative rate equations for dissolution and precipitation were given in Section 2 as Eqs. 2-23 and 2-24. The latter is reproduced here for comparison with the equivalent FORTRAN expression:

$$-v_j^{\text{rel}} = k_{-,1} + k_{-,2}\,\xi + \left(\frac{1}{2}\right)k_{-,3}\xi^2 \quad, \qquad (5\text{-}1)$$

which is programmed as

$$-\text{RRELRC(NRC,1)} = \text{RPK(1,NRC)}$$

$$+ \text{RPK(2,NRC)}*\text{ZI1}$$

$$+ 0.5*\text{RPK(3,NRC)}*\text{ZI1}**2 \quad. \qquad (5\text{-}2)$$

Here, RRELRC(NRC,1) is the relative rate of the NRCth reactant at the current point of reaction progress (ZI1). The rate constants RPK are read from the INPUT file. RPK(2,NRC) and

RPK(3,NRC) are usually not used; thus, they have constant relative rates.

5.1.2. Transition-State Theory Rate Law

The parameters are given in a summary equation where the relevant equation has been modified to include up to four terms on its right side, each corresponding to a different mechanism:

$$-v_j = f_j\,s_j \sum_{i=1}^{i_{T,j}} k_{-,i}\,q_{-,i}$$

$$\left[1 - \exp\left(A_{-,j}/\sigma_{ij}\,RT\right)\right] \quad. \qquad (5\text{-}3)$$

s_j is the total surface area of the phase dissolving in the jth irreversible reaction. The active surface area factor (f_j) represents the proportion of effective to total surface area. The number of parallel mechanisms is $i_{T,j}$. The rate constant is $k_{-,i}$, and the kinetic activity product is $q_{-,i}$ for the ith mechanism. Near equilibrium the rate is proportional to the thermodynamic affinity for the jth reaction. This is programmed as

$$-\text{RREAC(NRC,1)} = \text{FK(NRC)}*\text{SK(NRC)}$$

$$*\left(\sum_{I=1}^{\text{IPMECH(NRC)}} \text{RPK(I,NRC)QPFAC(I,NRC)}\right.$$

$$\left.*(1.0 - \text{EFAC(I,NRC)})\right) \quad, \qquad (5\text{-}4)$$

where

$$\text{QPFAC(I,NRC)}$$

$$= \prod_{N=1}^{\text{NPDACT(I,NRC)}} \text{ACT(NPDAC(N))}$$

$$*(\text{CPDAC(N,I,NRC)}) \quad. \qquad (5\text{-}5)$$

and

$$\text{EFAC(I,NRC)}$$

$$= \text{EXP(1000.}*\text{AFFRCT(NRC)}/(\text{CPSIGMA(I,NRC)}$$

$$*\text{RCONST}*\text{TEMPK})) \quad. \qquad (5\text{-}6)$$

QPFAC and EFAC are not actual arrays in the code, but are used here merely as logical devices. ACT(NS) is the thermodynamic activity of the

NSth aqueous species. NPDAC is an index array that the code creates by decoding UPDAC, a name array. UPDAC is read from INPUT, along with the active surface area factor (FK), the surface area (SK), rate constants (RPK) and activation energies (EACTP) for reference temperatures (TRKP), the number of mechanisms (IPMECH), and the kinetic stoichiometric factors (CPSIGMA). Note that this rate law is the only one for which temperature corrections are made to the input rate data. AFFRCT is the precipitation affinity (A_-) and is carried in the code in units of kcal/mol. The factor of 1000 in Eq. 5-6 converts this into calories. RCONST is the gas constant (cal/mol–K), and TEMPK is the absolute temperature (K).

5.1.3. Linear Rate Law

The equation for the linear rate law is

$$-v_j = f_j\, s_j\, k_- \quad . \qquad (5\text{-}7)$$

This rate law allows users to impose a rate (surface area normalized) of constant value, which is programmed as

– RREAC(NRC,1)

$$= \text{FK(NRC)}*\text{SK(NRC)}*\text{RPK(1,NRC)} \quad . \quad (5\text{-}8)$$

This is now the only case where a precipitation rate law differs in form from its dissolution counterpart. The dissolution rate law for NRK = 3 is

$$v_j = f_j\, s_j\left(k_{+,1} + k_{+,2}\, t^{-1/}\right) \quad , \qquad (5\text{-}9)$$

which includes a second (parabolic) term. This is programmed as

RREAC(NRC,1)

$$= \text{FK(NRC)}*\text{SK(NRC)}*(\text{ RPK(1,NRC)}$$

$$+ \text{ RPK(2,NRC)}*\text{TIME}**(0.5)\ ) \quad . \quad (5\text{-}10)$$

It would be a relatively simple matter to extend Eqs. 5-7 and/or 5-9 to include additional terms if desired.

5.1.4. Activity-Term Rate Law

The rate equation here is Eq. 3-3, modified to include the active surface area factor:

$$v_j = f_j\, s_j \sum_{i=1}^{i_{T,j}} k_{-,i} \prod_{k=1}^{k_{T,ji}} a_k^{n_{jik}} \quad . \qquad (5\text{-}11)$$

Here $i_{T,j}$ is the number of mechanistic terms in the jth irreversible reaction. $k_{T,ji}$ is the number of activity factors appearing in a term, and n_{jik} is the exponent of the activity of the kth species in the ith term. This is programmed as

– RREAC(NRC,1) = FK(NRC)*SK(NRC)

$$*\left(\sum_{i=1}^{\text{IPMECH(NRC)}} \text{RPK(I,NRC)}*\text{QFAC (I,NRC)}\right) \quad , \quad (5\text{-}12)$$

where

QFAC (I,NRC)

$$= \sum_{N=1}^{\text{NPDACT(I,NRC)}} \text{ACT(NPDAC(N))}$$

$$**\text{CPDAC(N,I,NRC)} \quad . \quad (5\text{-}13)$$

Here again, QFAC is not an array that is actually used in the program. The INPUT file parameters are essentially the same as those used in handling transition-state theory; however, their meaning is interpreted somewhat differently in this rate law.

5.2. INPUT File Modifications

The INPUT file information pertaining to each reactant is organized into a coherent block. A summary of the INPUT file structure for each block follows. Appendix A lists the relevant EQ6 variables. A description of the complete INPUT file is given by Wolery (1986a) in the *EQ6 User's Manual*.

The relevant portion of the INPUT file that begins with the line NRCT defines the total number of reactants for the run (NRCT) and ends with the last reactant block:

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EQ6 INPUT FILE

```
* ----------------------------------------------------------------------------

    NRCT                                          (12X,I2)

* ----------------------------------------------------------------------------

    Do NRC from 1 to NRCT:
      (UREAC(J,NRC), J = 1,3)                      (12X,3A6)
      JCODE(NRC), JREAC(NRC)                       (12X,I2,10X,I2)
      MORR(NRC), MODR(NRC)                         (2(12X,E12.5))

      If JCODE = 1 (solid solution reactant):
        Do I from 1 until UENDB(1,I,NRC) = "ENDIT."
          (UENDB(J,I,NRC), J = 1,3),
          RXBARB(I,NRC)                            (3X,3A6,3X,E12.5)

      If JCODE = 2 ("special" reactant):
        VREAC(NRC)                                 (12X,E12.5)
        Do I = from 1 until UESRB(I,NRC) = "ENDIT."
          UESRB(I,NRC),CESRB(I,NRC)                (3X,A6,3X,E12.5)

      NSK(NRC), SK(NRC), FK(NRC)                   (12X,I2,10X,E12.5,12X,E12.5)
      NRK(NRC), NRPK(NRC)                          (2(12X,I2))

* ----------------------------------------------------------------------------
* Forward direction rate law:

      If NRK = 1:
        RK(1,NRC), RK(2,NRC), RK(3,NRC)            (3(12X,E12.5))
      If NRK = 2:
        IMECH(NRC)                                 (12X,I2)
        Do I from 1 to IMECH:
          RK(I,NRC), TRK(I,NRC), EACT(I,NRC)       (12X,E12.5,12X,E12.5,12X,E12.5)
          NDACT(I,NRC), CSIGMA(I,NRC)              (12X,E12.5,12X,I2,22X,E12.5)
          Do N from 1 to NDACT:
            UDAC(N,I,NRC),CDAC(N,I,NRC)            (12X,A6,18X,E12.5)

      If NRK = 3:
        RK(1,NRC), RK(2,NRC), RK(3,NRC)            (3(12X,E12.5))

      If NRK = 4:
        MECH(NRC)                                  (12X,I2)
        Do I from 1 to IMECH:
          RK(I,NRC), NDACT(I,NRC)                  (12X,E12.5,12X,I2)
          Do N from 1 to NDACT:
            UDAC(N,I,NRC),CDAC(N,I,NRC)            (12X,A6,18X,E12.5)

* ----------------------------------------------------------------------------
* Backward direction rate law:

      If NRPK = -1, skip this section

      If NRPK = 1:
        RPK(1,NRC), RPK(2,NRC), RPK(3,NRC)         (3(12X,E12.5))
```

```
If NRPK = 2:
    IPMECH(NRC)                                        (12X,I2)
    Do I from 1 to IPMECH:
        RPK(I,NRC), TRKP(I,NRC), EACTP(I,NRC)          (12X,E12.5,12X,E12.5,12X,E12.5)
        NPDACT(I,NRC), CPSIGMA(I,NRC)                  (12X,E12.5,12X,I2,22X,E12.5)
        Do N from 1 to NPDACT:
            UPDAC(N,I,NRC),CPDAC(N,I,NRC)              (12X,A6,18X,E12.5)


If NRPK = 3:
    RPK(1,NRC)                                         (12X,E12.5)


If NRPK = 4:
    IPMECH(NRC)                                        (12X,I2)
    Do I from 1 to IPMECH:
        RPK(I,NRC), NPDACT(I,NRC)                      (12X,E12.5,12X,I2)
        Do N from 1 to NPDACT:
            UPDAC(N,I,NRC),CPDAC(N,I,NRC)              (12X,A6,18X,E12.5)

*  ------------------------------------------------------------------------------------
```

All rate constants, with the exception of some that appear in the activity-term rate law (e.g., k_4 in the rate law of Plummer et al., 1978) are to be input as positive values. FK, CSIGMA, and CPSIGMA values of zero default to unity. Note that the surface area, SK, is always entered, even when the surface area code is set for the option to maintain constant specific surface area (NSK = 1).

6. Test Problems

Three sample problems are presented in this section. The first demonstrates the numerical accuracy of the code and its ability to reproduce an experiment described in the literature. The second, which is used only to reproduce an experiment described in the literature, represents a case in which the effect of the changing chemical environment on the rate is more complex. The third is a model of a system with conditions known to occur in nature, yet not investigated in the laboratory. The use of selected experimental data in these test cases is for purposes of demonstration and does not necessarily constitute an acceptance of the interpretation of the experimental data by the authors of this report. Appendix B contains EQ3NR and EQ6 INPUT files for the sample problems.

6.1. Quartz Precipitation Kinetics

Rimstidt (1979) and Rimstidt and Barnes (1980) determined rate constants for the dissolution and precipitation of pure silica phases as a function of temperature (0 to 300°C), using a rate equation consistent with TST rate law. The rate constants reported for quartz sand, determined by direct laboratory measurement, were used to test TST algorithm programmed into EQ6. This test was done both to verify the numerical integration algorithm by comparison with a closed-form solution and to validate the rate model itself by comparison with the experimental data from which it was reportedly derived.

The Rimstidt and Barnes equation was discussed in Section 3.3. Their rate equation (Eq. 3-37) is equivalent to the forms programmed into the code (Eqs. 3-13 and 3-14). We actually used the dissolution form Eq. 3-13 in making the test calculations. The test case chosen corresponds to Run 2E at 105°C, an experiment reported by Rimstidt (1979) and Rimstidt and Barnes (1980), in which quartz was grown from supersaturated solution. The starting solution was distilled water, reported to contain 106.5 ppm SiO_2 (49.8 ppm Si), at 25°C. The figures reported by Rimstidt and

Barnes in both documents suggest that a more accurate value for the initial concentration is 101.0 ppm SiO_2 (47.2 ppm Si). After two hours, the initial starting concentration dropped to the lower value as reported by the authors.

The experimental data were compared with two values given for the rate constants at 105°C. The authors reported a value of k_+ that yielded the best fit to their data for this particular run. This value, 7.92×10^{-16} mol cm^{-2} s^{-1}, generated the upper curve in Fig. 1. The EQ3NR and EQ6 INPUT files used to generate this model are reproduced in Appendix B. The good fit in this case can be used to validate the TST model because the rate-constant values on which the calculation was based were derived from the same experimental data.

A closed-form solution to the Rimstidt and Barnes (1980) rate law was also computed (Appendix C). This solution was used to verify the correctness of the code's numerical integration procedure. The results show good agreement (Fig. 1).

A second rate-constant value at 105°C was computed using the temperature-dependent, least-squares regression equation reported by the authors. This equation was generated by using the authors' experimental data for relevant runs together with experimental data available in the literature. A value of k_+, 2.53×10^{-15} mol cm^{-2} s^{-1}, was computed from the following equation for k_+:

$$\log k_+ = 1.174 - 0.002028\,T - 4158/T \quad (6\text{-}1)$$

A similar equation is reported for k_-:

$$\log k_- = -0.707 - 2598/T \quad (6\text{-}2)$$

Following Eq. 3-18, with $m = 1$,

$$\log K_+ = 1.881 - 0.002028\,T - 1560/T \quad (6\text{-}3)$$

This rate-constant value was used to compute the lower curve in Fig. 1 and did a poor job of reproducing the experimental data.

The equilibrium constant used for quartz in these calculations was adjusted slightly from the value that would be calculated from the interpolation of polynomial coefficients in the EQ3/6 thermodynamic database. This adjustment, which was made using the NXMOD option, permitted consistency to be maintained between the EQ6 run
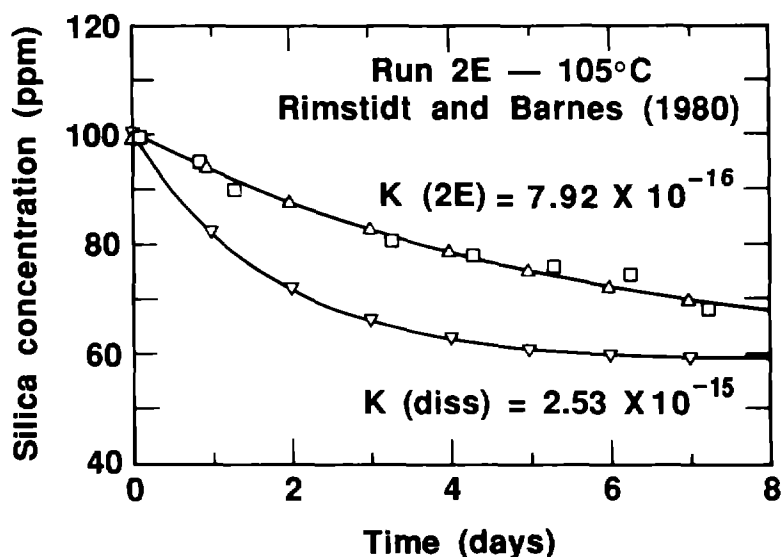
Figure 1. Precipitation growth kinetics of quartz in Run 2E reported Rimstidt (1979) and Rimstidt and Barnes (1980). Silica concentration in solution decreases as a function of time. Upper curve: Rimstidt–Barnes TST model with k_+ = 7.92 × 10^{-16} mol cm^{-2}s^{-1} (see text). Lower curve: same model with k_+ = 2.53 × 10^{-15} mol cm^{-2}s^{-1} (Eq. 6-1). Squares: Rimstidt and Barnes experimental data. Triangles: points calculated for closed-form solution (see Appendix C).

and Rimstidt and Barnes data for Eq. 6-3. A difference of about 9% was found in the values for K_+. A complete discussion of the NXMOD option is given by Wolery (1986a).

6.2. Calcite Precipitation Kinetics

Numerous reviews have been done on calcite precipitation kinetics (e.g., Plummer et al., 1979; House, 1981; Cassford et al., 1983; Morse, 1983). To demonstrate the use of EQ6 using the activity product term rate equations for calcite precipitation, the experimental data of Reddy et al. (1981) were used as an example. Reddy et al. prepared oversaturated solutions of calcite by equilibrating reagent-grade seed crystals at 4°C with distilled water and bubbling 100% CO_2 through the system. (This method was used because the solubility of calcite increases with decreasing temperature. Thus, subsequent heating develops an oversaturated solution). The solutions were then filtered and maintained at constant p_{CO2}, pH, and tem-

perature. With heating, the resulting solution was metastably oversaturated. The solution was seeded, and total calcium concentration in solution was determined as a function of time. The specific laboratory conditions for Run 7 were used as constraints for generating the EQ3NR and EQ6 input files listed in Appendix B.

Reddy et al. (1981) used Eq. 3-5 to interpret their experimental data:

$$v_i = s\left(k_1 a_{H^+}\right.$$

$$\left. + k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} + k_4 a_{Ca^{2+}} a_{HCO_3^-}\right) \quad . \quad (6\text{-}4)$$

The EQ6 rate-constant values, consistent with reaction progress on a millimole basis, are: $k_1 = 5.1 \times 10^{-5}$, $k_2 = 3.45 \times 10^{-8}$, and $k_3 = 1.19 \times 10^{-10}$. The value of k_4, specifically fit to the results of Run 7, was -3.1×10^{-5}.

Figure 2 shows the results of the EQ6 model calculations generated with the activity term rate
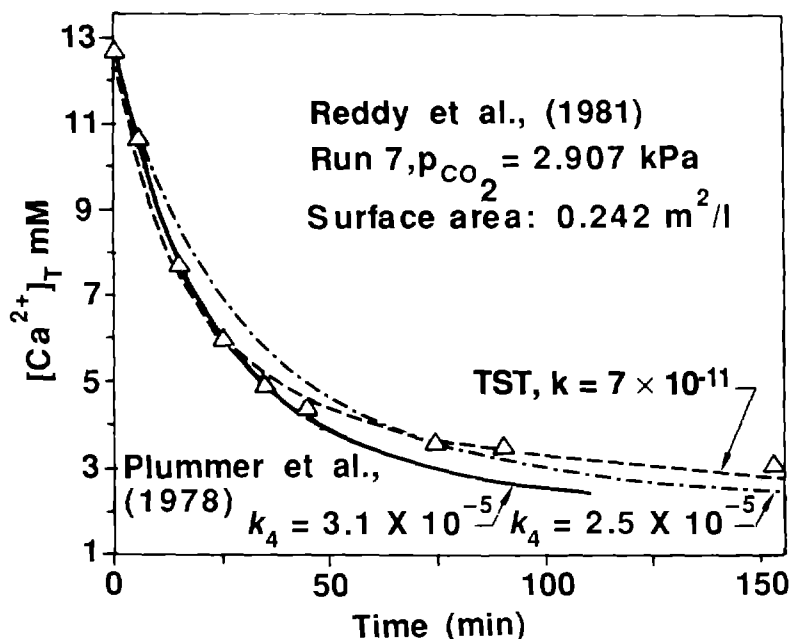
Figure 2. Experimental kinetic data for calcite precipitation in Run 7, from Reddy et al. (1981), is shown to decrease in total calcium concentration in solution as a function of time. The temperature is 25°C. The two lower curves show the results of EQ6 calculations for two values of k_4 using the activity-term rate law of Plummer et al. (1978). The upper curve was generated using a simple transition-state theory (TST) model (see text).

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law and the experimentally determined k_4 compared with the observed experimental data points. The figure also shows an additional run that was generated with the value for k_4 slightly increased to 2.5×10^{-5} to illustrate the sensitivity of the results to the k_4 parameter. The results of the same experiment are also shown in Fig. 2 using the EQ6 TST rate law. The results of the model calculation generated using a TST rate constant of $k_- = 7 \times 10^{-11}$ mol/cm^2-s and stoichiometric factor $\sigma = 1$ illustrate that both the activity term and the TST rate laws reproduce the experimental data by about the same degree of accuracy.

For comparison, the precipitation rate at each experimental point is determined by taking the slope of a smoothed curve going through the experimental points of Fig. 2. These data points were calculated by using the WATEQF computer code (Plummer et al., 1976) and plotted in Fig. 3 along with the EQ6 calculated rates.

6.3 Transformation of Cristobalite to Quartz

Quartz is the silica (SiO_2) phase that is thermodynamically stable at temperatures below 867°C. However, cristobalite can form metastably above 150°C and then undergo conversion to quartz. To illustrate this, we use an example in which cristobalite is converted to quartz at 250°C. Unlike the previous examples, this experiment is not carried out in the laboratory and represents an extrapolation of kinetic data. In this example, the initial solution is in equilibrium with cristobalite (708 ppm SiO_2), and supersaturated with respect to quartz. The quartz phase grows because the solution is supersaturated with respect to it (saturation is 180 ppm SiO_2). Silica is precipitated and removed from solution. This causes undersaturation with respect to cristobalite, which then dissolves and is transformed into quartz.
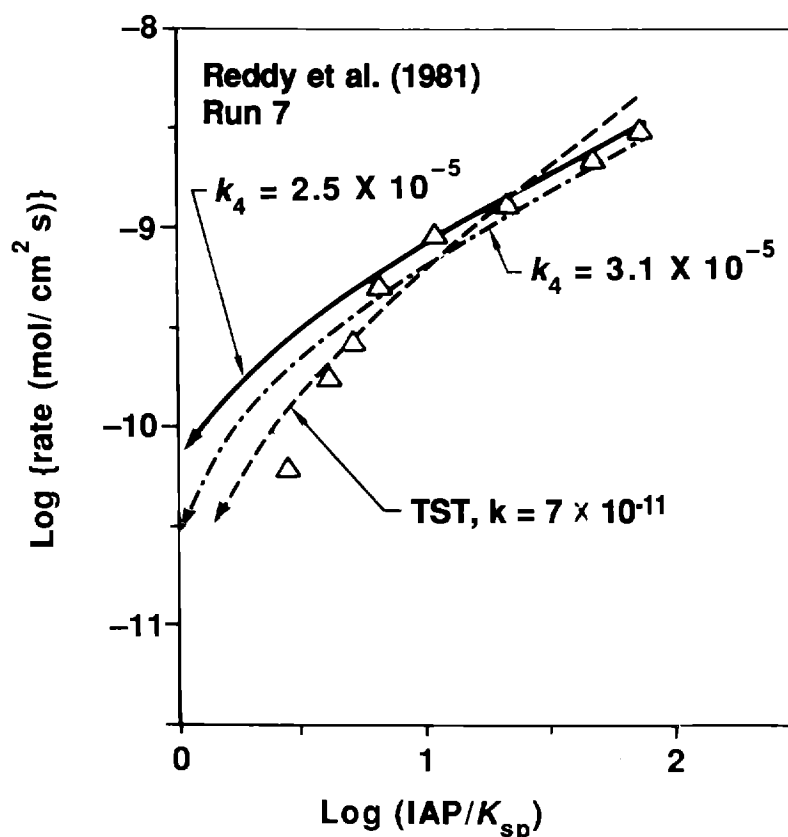
Figure 3. Experimental precipitation rates (triangles) as a function of calculated mineral saturation indices for calcite (from Reddy et al., 1981), and calculated EQ6 model results generated using the activity term and transition-state theory (TST) rate equations (see Fig. 2 caption and text).

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For this example, we used a closed system consisting of 1 kg H_2O, 1 g cristobalite, and a trace of quartz as seed material (about 0.6 mg). The rate constants for silica dissolution and precipitation, taken from Rimstidt and Barnes (1980), are: k_+ at 250°C is 1.5×10^{-12} for quartz and 3.6×10^{-12} for cristobalite. The specific surface areas of the two phases are treated as constants (NSK = 1). The total surface areas of the two solid phases vary as a function of time as the amounts of the solids vary during the run. We assume, for this example, that the specific surface area for both reactants is set to 500 cm²/g. The actual EQ6 surface area variables (SK) are 500 and 0.3 cm² for cristobalite and quartz, respectively. The test case was run for a time interval of 10 years. The results are shown in Figs. 4 and 5.

Over the first four years of the simulation, the solution composition is fairly constant. During this period, the affinity for dissolution of cristobalite is less than 0.02 kcal/mol and, for that reason, the dissolution rate is less than 3×10^{-6} mol/day. On the other hand, the affinity to precipitate quartz is greatest during the first four years of the run, starting at 0.636 kcal/mol and decreasing only to 0.616 kcal/mol by the end of four years. Because of the small surface area, the rate of quartz precipitation is low (less than 4×10^{-6} mol/day).

The rate of cristobalite dissolution reaches a maximum at about 6.5 years. Then, as this solid starts to disappear, its surface area decreases. By the end of the run, the dissolution rate is on the order of 10^{-7} mol/day, even through the affinity to dissolve is as much as 0.633 kcal/mol. For quartz, the maximum precipitation rate is reached at 6.5 years, also, because the surface area increases as more and more solid is formed. However, the solution also becomes less and less supersaturated. At the end of the run, the rate of quartz precipitation is only 2×10^{-7} mol/day, and the precipitation affinity is 0.002 kcal/mol. The time at which the rates reach their peak (corresponding also to the position of the inflection point in Fig. 4) depends on the amount of cristobalite available initially and on the value assigned to the specific surface. A caveat concerning the validity of this example should be pointed out. The present example was run at pH 6, well in the range of validity of the Rimstidt and Barnes (1980) rate model. There is some evidence, however, that the rates of silica dissolution are pH-dependent (Hurd, 1973).

Figure 4. Calculated silica concentration as a function of time for the transformation of cristobalite to quartz at 250°C. The initial solution is saturated with cristobalite (hence, supersaturated with quartz). The TST rate law and constants of Rimstidt (1979) and Rimstidt and Barnes (1980) were used in this EQ6 simulation.

Figure 5. Masses of silica phases calculated by EQ6, plotted as a function of time, for the transformation of cristobalite to quartz at 250°C. The initial system contained 1 g of cristobalite. The curves were generated using the TST rate law and rate constants of Rimstidt (1979) and Rimstidt and Barnes (1980).

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Acknowledgments

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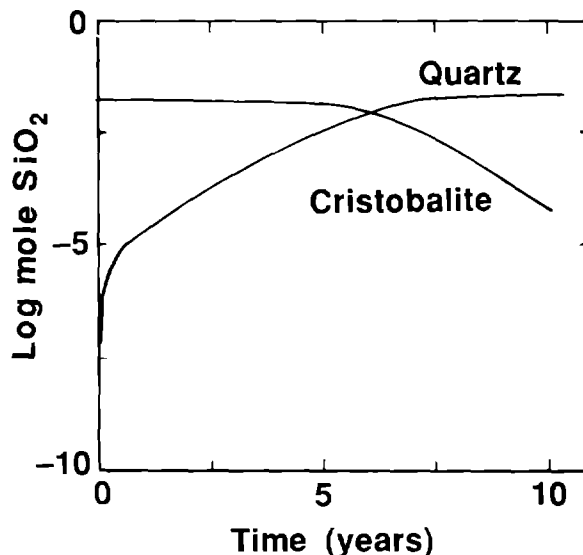Aagaard, P., and H. C. Helgeson (1982), "Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions—I. Theoretical Considerations," *Amer. J. Sci.* **282**, 237–285.

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Appendix A. List of Relevant FORTRAN Variables

This list includes only major variables added to the EQ6 code as a result of the addition of the precipitation kinetics option, as well as others that are included for the sake of completeness. A complete list of all variables can be found in the *EQ6 User's Guide* (Wolery, 1986a). The designation "INPUT:" refers to a parameter that is read from the INPUT file.

AFFRCT   Reaction affinity (A_-, kcal/mol).

CDAC   INPUT: Integer exponent of the activity of an aqueous species, specified in a dissolution rate law.

CESRB   INPUT: number of moles of element UESRB per mole of "special" reactant.

CPDAC   INPUT: Integer exponent of the activity of an aqueous species, specified in a rate law for precipitation.

CSIGMA   INPUT: σ, appearing in a dissolution rate law.

CPSIGM   INPUT: σ, appearing in a precipitation rate law.

EACT   INPUT: $E_{a,+}$, activation energy for the forward direction.

EACTP   INPUT: $E_{a,-}$, activation energy for the reverse direction.

FK   INPUT: f, active surface area factor.

IMCHMX   Maximum allowed number of terms (mechanisms) in a rate law.

IMECH   INPUT: The number of terms in a dissolution rate law.

IOPT1   INPUT: Option switch for setting kinetic mode (IOPT1 = 1).

IPMECH   INPUT: The number of terms (mechanisms) in a precipitation rate law.

JCODE   INPUT: Flag denoting the type of reactant:
- = 0 Mineral
- = 1 Solid Solution
- = 2 "Special" Reactant
- = 3 Aqueous Species
- = 4 Gas Species.

JREAC   INPUT: Flag for each reactant:
- = 0 Set to react
- = -1 Saturated but continues reacting
- = 1 Exhausted
- = -2 Saturated, any remaining mass has been transferred to the equilibrium subsystem.

MORR   INPUT: Moles of reactant at the beginning of the run.

MODR   INPUT: Moles of reactant previously destroyed.

NDAC   The index of an aqueous species whose activity appears in a rate law for dissolution.

NDACT   INPUT: The number of activities appearing in a term (mechanism) of a rate law for dissolution.

NDCTMX   Maximum allowed number of species whose activities can appear as a factor in a rate-law term.

NMCHK   Flag for each solid in the database involved in the calculations:
- = 0 The solid is not a reactant with precipitation kinetics (i.e., either the solid is not a reactant or, if it is a reactant, it has NRPK = 0)
- = 1 The solid is a reactant with precipitation kinetics (i.e., with NRPK >0).

NPDAC   The index of an aqueous species whose activity appears in a rate law for precipitation.

NPDACT   INPUT: The number of activities appearing in a term (mechanism) of a rate law for precipitation.

NRC   Reactant index parameter.

NRCT   INPUT: Number of reactants.

NRCTMX   Maximum allowed number of reactants.

NRK   INPUT: Rate law code for reactant dissolution:
- = 1 Relative rate law
- = 2 Transition-state theory rate law
- = 3 Linear plus parabolic rate law
- = 4 Activity-term rate law.

NRPK   INPUT: Rate law code for reactant precipitation:
           = -1 Use the specified dissolution rate law (NRK must be 2 or 4)
           =   0 Instantaneous equilibrium precipitation
           =   1 Relative rate law
           =   2 Transition-state theory rate law
           =   3 Linear (constant) rate law
           =   4 Activity-term rate law.
NSK   INPUT: Reactant surface area option switch:
           =   0 Constant surface area
           =   1 Constant specific surface area.
NSRT   Number of "special" reactants (i.e., reactants with JCODE = 2).
NSRTMX   Maximum allowed number of "special" reactants.
NXCHK   Flag for each solid solution in the data base involved in the calculations:
           =   0 The solid solution is not a reactant with precipitation kinetics (i.e., either
               the solid solution is not a reactant or, if it is a reactant, it has NRPK = 0)
           =   1 The solid solution is a reactant with precipitation kinetics (i.e., with
               NRPKT >0).
NXRT   The number of solid-solution reactants.
NXRTMX   Maximum allowed number of solid-solution reactants.
RCONST   The gas constant = 1.98726 cal mol^{-1}K^{-1} (= 8.314 J mol^{-1}K^{-1}).
RIREAC   The inverse rate $(dt/d\xi)$.
RK   INPUT: Rate constant or parameter for a dissolution rate law (dimensionless for relative
           rates, otherwise mol/cm^2-s).
RPK   INPUT: Rate constant or parameter for a precipitation rate law (dimensionless for relative
           rates, otherwise mol/cm^2-s).
RREAC   Rate of a reaction (mol/s).
RRELRC   The relative rate of a reaction $(d\xi_j/d\xi)$.
RXBARB   Input: The mole fraction of an end-member mineral in a solid solution reactant.
SK   INPUT: Surface area of a reactant mineral (cm^2).
SSK   Specific surface area of a reactant (cm^2/mol).
TRK   INPUT: Temperature (°C) corresponding to rate constant value in RK and activation
           energy in EACT.
TRPK   INPUT: Temperature (°C) corresponding to rate constant value in RKP and activation
           energy in EACTP.
TEMPC   Temperature (°C); calculated from TEMPC0, TK1, TK2, and TK3; see Wolery, 1986a.
TEMPC0   INPUT: Temperature (°C) at ξ = 0.
TEMPK   Temperature (K).
TIME   Time (s).
TIMEMX   INPUT: The maximum value of model time (s); the run terminates when TIME exceeds
           TIMEMX.
TK1,TK2,
TK3   INPUT: Parameters for temperature variation during the run.
TRATE   Overall reaction rate: sum of absolute values of RREAC for reactants with either NRK or
           NRPK greater than 1.
TSTRT   INPUT: The value of time (s) at the start of the run.
UDAC   INPUT: The name of an aqueous species whose activity appears in a rate law for
           dissolution.
UENDB   INPUT: Name of a pure mineral end member of a solid solution reactant.
UESRB   INPUT: Name of a chemical element in a "special" reactant (i.e., in a reactant with
           JCODE = 2).
UPDAC   INPUT: Name of an aqueous species whose activity appears in a rate law for
           precipitation.
UREAC   INPUT: Name of a reactant.
VREAC   INPUT: The molar volume of a reactant (cm^3/mol).

ZI1   Overall reaction progress variable, ξ.

ZISTRT INPUT: The value of ZI1 at the start of the run.

ZIMAX   INPUT: The maximum allowed value of ZI1 in the run.

Appendix B.   Input Files for Test Problems

EQ3NR INPUT FILE FOR TEST PROBLEM #1

EQ3NR INPUT file: i3sio2   09/25/84   J.M. Delany + I. Puigdomenech

 SUPERSATURATED QUARTZ SOLUTION, 25°C, pH determined by electrical balance

 Initial solution : distilled water + 101.0 ppm sio2(aq).

 Silica phases less stable than quartz have been suppressed.

 Reference: Run 2e
            Rimstidt (1979; pp. 62, 65, and 117 and Fig. 14)
            Rimstidt and Barnes (1980; pp. 1687 and 1688 and Fig.2)
endit.
     tempc=   25.
       rho=   1.00000   tdspkg=   0.   tdspl=   0.
       fep=   -0.68   uredox=
     tolbt=   0.   toldl=   0.   tolsat=   0.
    itermx= 0
   iopt1-10=   0   1   0   0   0   0   0   0   0   0
   iopg1-10=   0   0   0   0   0   0   0   0   0   0
   iopr1-10=   0   0   1   -2   0   0   0   0   0   0
   iodb1-10=   0   0   0   0   0   0   0   0   0   0
     uebal= h+   uacion=
     nxmod= 4
   species= tridymite
      type= 1   option= -1
   species= chalcedony
      type= 1   option= -1
   species= amorphous silica
      type= 1   option= -1
   species= cristobalite
      type= 1   option= -1
                h+   -8.8   16
                sio2(aq)   101.0   2
     endit.

EQ6 INPUT FILE FOR SAMPLE PROBLEM #1

EQ6 INPUT file: i6sio2   09/25/84   J.M. Delany + I. Puigdomenech

  EQ6 SIMULATION OF RUN 2E, 105°C, duration 8 days.

  Initial solution: generated by EQ3NR input file i3sio2.

  Reactant: quartz sand
              morr (moles of reactant) calculated from a/m = 261 and
              bet measurements = .92e-2 m2/g reported for quartz sand.
             rate constants from the master regression equation:
              k(-)(quartz) = 2.65e-12
              k(+)(quartz) = 2.53e-15
             specific rate constants for run 2e:
              k(-)(quartz, run 2e) = 8.15e-13
              k(+)(quartz, run 2e) = 7.92e-16
  Reference:
             Rimstidt (1979; pp. 62, 65, and 117 and Fig.14)
             Rimstidt and Barnes (1980; pp. 1687 and 1688 and Fig.2)
endit.
    nmod11= 2   nmod12= 0
    tempc0=   105.   jtemp= 0
       tk1=   0.   tk2=   0.   tk3=   0.
    zistrt=   0.   zimax=   1.
     tstrt=   0.   timemx=   692000.
    kstpmx=   500   cplim=   0.
     dzprn=   dzprlg=   0.5   ksppmx=   5
    dzplot=   1.e+10   dzpllg=   1.e+10   ksplmx= 10000
     ifile= 60
  iopt1-10=   1   0   0   0   0   0   0   0   0   0
     11-20=   0   0   0   0   0   0   0   0   0   0
  iopr1-10=   0   0   0   0   0   0   0   1   0   0
     11-20=   0   0   0   0   0   0   0   0   0   0
  iodb1-10=   0   0   0   0   0   0   0   0   0   0
     11-20=   0   0   0   0   0   0   0   0   0   0
     nxopt= 0
      nffg= 0
      nrct= 1
*--
reactant= quartz
     jcode= 0   jreac= 0
      morr=   472.   modr=   0.
       nsk= 0   sk=   2612800.   fk=   1.
       nrk= 2   nrpk= -1
     imech= 1
       rk1=   7.92e-16   trk1=   105.   eactp1=   0.
     ndact= 0   csigma=   1.
*--

```
*              take the defaults for parameters in this block
*                     by entering zeros or blanks
   dlzidp=          0.
    tolbt=          0.        toldl=          0.      tolx=          0.
   tolsat=          0.        tolsst=         0.
   screwl=          0.        screw2=         0.      screw3=        0.
   screw4=          0.        screw5=         0.      screw6=        0.
   zklogu=          0.        zklogl=         0.
   dlzmxl=          0.        dlzmx2=         0.
   itermx=  0                 ntrymx=  0
 * npslmx=  0                 nsslmx=  0
 *_____
* following is the pickup file written by eq3nr
* pickup file written by eq3nr.3245c51
*  supported by eqlib.3245c41
EQ3NR INPUT file: i3sio2      09/25/84      J.M. Delany + I. Puigdomenech

 SUPERSATURATED QUARTZ SOLUTION, 25°C, pH determined by electrical balance

 Initial solution : distilled water + 101.0 ppm sio2(aq).

 Silica phases less stable than quartz have been suppressed.

 Reference:  Run 2e
             Rimstidt (1979; pp. 62, 65, and 117 and Fig. 14)
             Rimstidt and Barnes (1980; pp. 1687 and 1688 and Fig.2)
endit.
   uacion= none
   tempci=  2.50000e+01
    nxmod=  5
 species= quartz
    type=  1                option=  1               xlkmod= -3.0126
 species= tridymite
    type=  1                option= -1
 species= chalcedony
    type=  1                option= -1
 species= amorphous silica
    type=  1                option= -1
 species= cristobalite
    type=  1                option= -1
    iopg1=  0                  iopg2=  0               iopg3=  0
    iopg4=  0                  iopg5=  0               iopg6=  0
    iopg7=  0                  iopg8=  0               iopg9=  0
   iopg10=  0
      kct=  3                    ksq=  4                 kgmt=  4
      kmt=  6                    kxt=  6                 kdim=  6
     kprs=  0
 o                 5.551466572315803e+01
 si                1.680979961387399e-03
 h                 1.110185983062261e+02
 electr            8.809142651444724e-20
 h2o      h2o                 1.744365733541422e+00
 sio2(aq) sio2(aq)           -2.774609379623442e+00
 h+       h+                 -6.167207439820658e+00
 o2(g)    o2(g)              -1.000000000000001e-01
 xisteq                      -5.000000000000000e+02
 xi                          -6.167207439820658e+00
```

EQ3NR INPUT file: i3plum7   09/14/84   J. Delany + I. Puigdomenech

  SUPERSATURATED CALCITE SOLUTION, 25°C, pH determined by electrical balance.

  Initial solution: pco2= 0.0287 atm (3%), initial Ca= 12.732 mmol/l.

  The equilibrium constants used by Reddy et al. were input into
  EQ3/6 in order to more easily evaluate the experimental simulation.

  Reference: Run #7
             Reddy et al. (1981)

endit.
```
     tempc=          25.
       rho=           1.0     tdspkg=          0.      tdspl=          0.
       fep=          -0.68    uredox=
     tolbt=           0.      toldl=           0.      tolsat=         0.
     itermx=  0
   iopt1-10=      0    0    0    0    0    0    0    0    0    0
   iopg1-10=      0    0    0    0    0    0    0    0    0    0
   iopr1-10=      0    0    1   -2    0    0    0    0    0    0
   iodb1-10=      0    0    0    0    0    0    0    0    0    0
     uebal= h+                uacion=
     nxmod=  8
   species= hco3-
       type=  0               option=  0               xlkmod=  -10.330
   species= h2co3
       type=  0               option=  0               xlkmod=  -16.681
   species= caco3
       type=  0               option=  0               xlkmod=  -3.153
   species= cahco3+
       type=  0               option=  0               xlkmod=  -11.345
   species= calcite
       type=  1               option=  0               xlkmod=  -8.475
   species= co2(g)
       type=  2               option=  0               xlkmod=  -18.147
   species= ca(oh)+
       type=  0               option= -1
   species= aragonite
       type=  1               option= -1
                 ca++              12.732e-3     0
                 h+                    -7.00    16
                 hco3-             -1.542118    21     co2(g)
   endit.
```

EQ6 INPUT FILE FOR TEST PROBLEM #2

EQ6 INPUT file: i6plum7   09/14/84   J. Delany + I. Puigdomenech

EQ6 SIMULATION OF EXPERIMENT 7.

Initial solution: generated by EQ3NR input file i3plum7.

Reactant: baker reagent-grade calcite seeds
                              BET Ar. surface area= 0.228 m2/g
                              seed concentration= 1.06 g/l

Reference: experiment #7
            Reddy et al. (1981)
endit.
  nmodl1= 2   nmodl2= 0
  tempc0=   25.   jtemp= 0
     tk1=   0.   tk2=   0.   tk3=   0.
  zistrt=   0.   zimax=   0.0150
   tstrt=   0.   timemx=   9300.0
  kstpmx=   500   cplim=   0.0
  dzprnt=   0.0001   dzprlg=   10.   ksppmx= 10000
  dzplot=   0.   dzpllg=   0.   ksppmx=   0
   ifile= 60
iopt1-10=   1   0   0   0   0   0   0   0   0   0
   11-20=   0   0   0   0   0   0   0   0   0   0
iopr1-10=   0   0   0   0   0   0   0   1   0   0
   11-20=   0   0   0   0   0   0   0   0   0   0
iodb1-10=   0   0   0   0   0   0   0   0   0   0
   11-20=   0   0   0   0   0   0   0   0   0   0
   nxopt= 0
    nffg= 1
    uffg= co2(g)   moffg= 0.1   xlkffg= -1.542118
    nrct= 1
*---
reactant= calcite
   jcode= 0   jreac= 0
    morr=   0.01019   modr=   0.
     nsk= 0   sk=   2416.8   fk=   1.
     nrk= 4   nrpk= -1
   imech= 4
     rk1=   5.1e-05   trk1=   25.   eactp1=   0.
   ndact= 1
 species= h+   cdac=   1.0
     rk2=   3.45e-08   trk2=   25.   eactp2=   0.
   ndact= 1
 species= h2co3   cdac=   1.0
     rk3=   1.19e-10   trk3=   25.   eactp3=   0.
   ndact= 0
     rk4=   -3.1e-05   trk4=   25.   eactp4=   0.
   ndact= 2
 species= ca++   cdac=   1.0

```
   species= hco3-              cdac=          1.0
*----------------------------------------------------------------------
   dlzidp=              0.
    tolbt=              0.    toldl=          0.    tolx=          0.
   tolsat=              0.    tolsst=         0.
   screwl=              0.    screw2=         0.    screw3=        0.
   screw4=              0.    screw5=         0.    screw6=        0.
   zklogu=              0.    zklogl=         0.
   dlzmxl=              0.    dlzmx2=         0.
   itermx=  0                 ntrymx=  0
   npslmx=  0                 nsslmx=  0
*  pickup file written by eq3nr.3245c51
*  supported by eqlib.3245c41
EQ3NR INPUT file: i3plum7        09/14/84        J. Delany + I. Puigdomenech

   SUPERSATURATED CALCITE SOLUTION, 25°C, pH determined by electrical balance.

   Initial solution:  pco2= 0.0287 atm (3%), initial Ca= 12.732 mmol/l.

   The equilibrium constants used by reddy et. al. were input into
   EQ3/6 in order to more easily evaluate the experimental simulation.

   Reference: Run #7
              Reddy et al. (1981)

endit.
   uacion= none
   tempci=  2.50000e+01
    nxmod=  8
   species= hco3-
       type=  0            option=  1            xlkmod= -1.90000e-03
   species= h2co3
       type=  0            option=  1            xlkmod= -5.46456e-03
   species= caco3
       type=  0            option=  1            xlkmod=  4.52702e-02
   species= cahco3+
       type=  0            option=  1            xlkmod=  2.33196e-01
   species= ca(oh)+
       type=  0            option= -1            xlkmod=  0.
   species= calcite
       type=  1            option=  1            xlkmod=  4.99000e-02
   species= aragonite
       type=  1            option= -1            xlkmod=  0.
   species= co2(g)
       type=  2            option=  1            xlkmod=  1.56000e-02
     iopg1=  0              iopg2=  0              iopg3=  0
     iopg4=  0              iopg5=  0              iopg6=  0
     iopg7=  0              iopg8=  0              iopg9=  0
    iopg10=  0
       kct=  4                ksq=  5              kgmt=  5
       kmt=  7                kxt=  7              kdim=  7
      kprs=  0
   o                 5.558785910974166e+01
   ca                1.273200000000008e-02
```

```
h                          1.110451581601660e+02
c                          2.601272144693767e-02
electr            -2.442490654175344e-15
h2o        h2o             1.744365733541422e+00
ca++       ca++           -1.958771044283566e+00
h+         h+             -7.592622425036836e+00
co3--      co3--          -4.089288141210062e+00
o2(g)      o2(g)          -6.799999999999997e-01
xisteq                    -5.000000000000000e+02
xi                        -1.462646384564366e+00
```

EQ3NR INPUT FILE FOR TEST PROBLEM #3

EQ3NR INPUT file: i3si2   10/26/84   J.M. Delany + I. Puigdomenech

  SATURATED CRISTOBALITE SOLUTION, 250°C, pH=6.

  Silica phases other than cristobalite and quartz have been suppressed.

```
endit.
    tempc=          250.
      rho=            1.0    tdspkg=              0.      tdspl=              0.
      fep=           -0.7    uredox=
    tolbt=             0.     toldl=              0.      tolsat=             0.
   itermx= 30
  ioptl-10=      0    0    0    0    0    0    0    0    0    0
  iopgl-10=      0    0    0    0    0    0    0    0    0    0
  ioprl-10=      0    0    0    0    0    0    0    0    0    0
  iodbl-10=      0    0    0    0    0    0    0    0    0    0
    uebal=               uacion=
    nxmod=   3
  species= amorphous silica
     type=  1              option= -1                    xlkmod=  0.
  species= chalcedony
     type=  1              option= -1                    xlkmod=  0.
  species= tridymite
     type=  1              option= -1                    xlkmod=  0.
               h+                      -6.0    16
               sio2(aq)                 0.     19    cristobalite
   endit.
```

EQ6 INPUT FILE FOR TEST PROBLEM #3

EQ6 INPUT file: i6si2   10/26/84   J.M. Delany + I. Puigdomenech

  CRISTOBALITE TO QUARTZ TRANSFORMATION, 250°C.

  Initial solution: generated by EQ3NR input file i3si2.

  Reactant: cristobalite
                        seed concentration = 1.0 g/l
                        specific surface area = 0.05 m2/g
                        k(+) = 3.6e-12 (at 250°C)
            quartz:
                        trace concentration = .0006 g/l
                        specific surface area = 0.05 m2/g
                        k(+) = 1.5e-12 (at 250°C)

              Rate constants calculated from Rimstidt and Barnes (1980)

  Reference: Sosman (1965)

endit.
```
     nmodl1=  2                 nmodl2=  0
     tempc0=          250.      jtemp=   0
        tk1=            0.          tk2=            0.        tk3=            0.
     zistrt=            0.       zimax=            1.
      tstrt=            0.      timemx=      1.58e+8
     kstpmx=          500       cplim=            0.
      dzprn=                    dzprlg=          0.5       ksppmx=       5
     dzplot=        1.e+10      dzpllg=        1.e+10      ksplmx= 10000
      ifile= 60
    iopt1-10=    1    0    0    0    0    0    0    0    0    0
      11-20=     0    0    0    0    0    0    0    0    0    0
    iopr1-10=    0    0    0    0    0    0    0    1    0    0
      11-20=     0    0    0    0    0    0    0    0    0    0
    iodb1-10=    0    0    0    0    0    0    0    0    0    0
      11-20=     0    0    0    0    0    0    0    0    0    0
      nxopt=  0
       nffg=  0
       nrct=  2
*------------------------------------------------------------------------
  reactant= cristobalite
      jcode=  0                 jreac=  0
       morr=       0.01664       modr=           0.
        nsk=  1                    sk=          500.        fk=            1.
        nrk=  2                  nrpk=  -1
      imech=  1
        rk1=       3.6e-12       trk1=          250.      eactp1=          0.
      ndact=  0                 csigma=           1.
*------------------------------------------------------------------------
  reactant= quartz
      jcode=  0                 jreac=  0
```

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```
     morr=       0.00001      modr=          0.
      nsk=  1                   sk=       0.3004      fk=          1.
      nrk=  2                 nrpk=  -1
    imech=  1
      rkl=       1.5e-12       trkl=         250.   eactpl=         0.
    ndact=  0                csigma=          1.
*-----------------------------------------------------------------
*            take the defaults for parameters in this block
*                  by entering zeros or blanks
   dlzidp=        0.
    tolbt=        0.        toldl=          0.     tolx=         0.
   tolsat=        0.       tolsst=          0.
   screwl=        0.       screw2=          0.    screw3=         0.
   screw4=        0.       screw5=          0.
    zklogu=       0.        zklogl=         0.
   dlzmxl=        0.       dlzmx2=          0.
    itermx= 0               ntrymx=  0
   npslmx= 0               nsslmx=  0
*-----------------------------------------------------------------
* pickup file written by eq3nr.3245c33
*  supported by eqlib.3245c28
EQ3NR INPUT file: i3si2        10/26/84        J.M. Delany + I. Puigdomenech

  SATURATED CRISTOBALITE SOLUTION,  250°C, pH=6.

  Silica phases other than cristobalite and quartz have been suppressed.

endit.
    uacion= none
    tempci=  2.50000e+02
     nxmod=  3
   species= amorphous silica
      type=  1              option= -1             xlkmod=  0.
   species= chalcedony
      type=  1              option= -1             xlkmod=  0.
   species= tridymite
      type=  1              option= -1             xlkmod=  0.
    iopgl=  0              iopg2=  0               iopg3=  0
    iopg4=  0              iopg5=  0               iopg6=  0
    iopg7=  0              iopg8=  0               iopg9=  0
   iopgl0=  0
      kct=  3                ksq=  4               kgmt=  4
      kmt=  6                kxt=  6               kdim=  6
     kprs=  0
   o               5.553375340345201e+01
   si              1.178568843509342e-02
   h               1.110186093002230e+02
   electr         -8.692554691523756e-06
   h2o        h2o               1.744365733541422e+00
   sio2(aq)   sio2(aq)         -1.928699999687495e+00
   h+         h+               -5.997754326575489e+00
   o2(g)      o2(g)            -6.999999999999993e-01
   xisteq                      -5.000000000000000e+02
   xi                          -5.271527587215132e+00
```

References

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Rimstidt, J. D. (1979), *The Kinetics of Silica-Water Reactions*, Ph. D. Thesis, Pennsylvania State University.

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Sosman, R. B. (1965), *The Phases of Silica* (Rutgers University Press, New Brunswick, NJ), 388 p.

Wolery, T. J. (1986a), *EQ6, A Computer Program for Reaction-Path Modeling of Aqueous Geochemical Systems: User's Guide and Documentation*, draft, Lawrence Livermore National Laboratory, Livermore, CA.

Appendix C. Example of Closed-Form Solutions for SiO$_2$

In simple cases, where closed-form solutions are obtainable, the results can be compared with results obtained from numerical integration calculations. Relative rates, constant rates, and time functions generally yield closed-form integrations quite readily. However, they are not realistic in most cases. Transition-state theory (TST) can be reduced in some cases to a mathematical formulation for which closed-form solutions are obtainable. In Section 3.3, we discussed the Rimstidt-Barnes (1980) rate law for silica dissolution and precipitation. Assuming the conditions under which this rate law is valid, it can be written in the form

$$dm/dt = \left(\frac{s}{w_w}\right)k_+\left(1 - \frac{m}{K'_+}\right) \quad . \tag{C-1}$$

A closed-form solution to this equation can be obtained if s, w_w, k_+, and K'_+ are all constant. For most reaction scenarios involving only precipitation and/or dissolution of pure silica phases, as in the experiments of Rimstidt and Barnes, these parameters are likely to vary by only very small amounts. Equation C-1 can be recast in the form

$$dm/dt = A - Bm \quad , \tag{C-2}$$

where A and B are constants defined by

$$A = \left(\frac{s}{w_w}\right)k_+ \tag{C-3}$$

and

$$B = A/K'_+ \quad . \tag{C-4}$$

To solve Eq. C-2, we must specify an initial condition. Let m° be the value of m at $t = 0$. We know that the value must be m^{eq} at $t = \infty$ because we expect equilibrium to be approached. This is given by

$$m^{eq} = K'_+ \tag{C-5}$$

The solution to the differential equation C-2 is

$$m = \left(\frac{A}{B}\right) + \left(\frac{A}{B} - m^\circ\right)e^{-Bt} \quad . \tag{C-6}$$

This can also be written as

$$m = m^{eq} + \left(m^\circ - m^{eq}\right)e^{-Bt} \quad . \tag{C-7}$$

The chief feature of this equation is that the difference between the final and initial values of m decays exponentially. Note that the time required to actually reach equilibrium is infinity.

If two silica phases (1 and 2) are reacting with an aqueous solution, the net rate equation yielding the total rate of change of concentration is

$$dm/dt = dm/dt|_1 + dm/dt|_2 \quad . \tag{C-8}$$

If A and B are redefined as

$$A = A_1 + A_2 \tag{C-9}$$

and

$$B = B_1 + B_2 \quad , \tag{C-10}$$

the form of Eq. C-8 reduces to the form of Eq. C-2. A_1 and A_2 are defined according to Eq. C-3, using parameters for the appropriate phase, and B_1 and B_2 are similarly defined using Eq. C-4. Because steady state can be defined as $dm/dt = 0$, the concentration at steady state is

$$m^{ss} = \frac{A}{B} \quad . \tag{C-11}$$

For the case of a single phase, $m^{ss} = m^{eq}$. Now, however, m^{ss} can be written as

$$m^{ss} = \frac{A_1 + A_2}{\left(\dfrac{A_1}{m_1^{eq}} + \dfrac{A_2}{m_2^{eq}} \right)} \quad . \tag{C-12}$$

If A_1 is much greater than A_2, then m^{ss} will be close to m^{eq} for phase 1. On the other hand, if A_2 is much greater than A_1, then m^{ss} will be close to m^{eq} for phase 2. The general solution, Eq. C-6, can be written in this case as

$$m = m^{ss} + \left(m^{ss} - m^o \right) e^{-Bt} \quad . \tag{C-13}$$

Because the surface areas of the above phases are treated as constants, this two-phase model is intuitively unrealistic. In a real system, equilibrium with the most stable phase is expected. We will now consider a case in which the specific surface area ($s_{\#}$) is kept constant. The surface area is given by

$$s = s_{\#} M_s n_s \quad , \tag{C-14}$$

where M_s is the molecular weight of the solid and n_s is the number of mols of the solid present. Mass balance requires that

$$n_s = n_s^o + w_w \left(m^o - m \right) \quad , \tag{C-15}$$

where n_s^o is the value of n_s at $t = 0$. Substituting Eq. C-15 into Eq. C-14, and then into Eq. C-1, yields

$$dm/dt = C \left(A - m \right) \left(B - m \right) \quad , \tag{C-16}$$

where

$$C = \frac{k_+ M_s s_{\#}}{K_+} \quad , \tag{C-17}$$

$$A = \frac{n_s^o}{w_w} + m^o \quad , \tag{C-18}$$

and

$$B = K_+^{'} \quad . \tag{C-19}$$

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A solution to Eq. C-19 for the case $m^\circ = 0$ is given by Margenau and Murphy (1956):

$$m = \frac{A\left(1 - e^{(A-B)Ct}\right)}{\left(1 - \dfrac{A}{B}\, e^{(A-B)Ct}\right)} \quad . \tag{C-20}$$

If $A = B$, this solution does not work. A more general solution is

$$m = \frac{A\left(1 - \left(\dfrac{A - m^\circ}{B - m^\circ}\right)\left(\dfrac{B}{A}\right)e^{(A-B)Ct}\right)}{\left(1 - \left(\dfrac{m^\circ - A}{m^\circ - B}\right)e^{(A-B)Ct}\right)} \quad , \tag{C-21}$$

which also fails to work when $A = B$. However, m° is not restricted to a value of zero.

References

Margenau, H., and G. M. Murphy (1956), *The Mathematics of Physics and Chemistry*, Second Edition, (D. Van Nostrand Company, Inc., New York), p. 55.

Rimstidt, J. D., and H. L. Barnes (1980), "The Kinetics of Silica-Water Reactions," *Geochim. Cosmochim. Acta* **44**, 57.

SPS/sb